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Date: August 26, 1976

Project Title: An Investigation of OH Reactions of Importance in the Perturbed Troposphere

Project No: B-473

Project Director: Dr. D. D. Davis

Sponsor: Environmental Protection Agency; Research Triangle Park, N.C. 27711

Agreement Period: From July 25, 1976 Until July 24, 1977

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Sponsor Contact Person (s):

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Assigned to: Applied Sciences Laboratory (School/Laboratory)

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SPONSORED PROJECT TERMINATION

Posted 8/31/77

Date: August 30, 1977

Project Title: An Investigation of OH Reactions of Importance in the Perturbed Troposphere

Project No: B-473

Project Director: Dr. D. D. Davis

Sponsor: Environmental Protection Agency; Research Triangle Park, NC 27711

Effective Termination Date: 7/24/77

Clearance of Accounting Charges: 7/24/77

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CA—4 (3/76)

B-473

AN INVESTIGATION OF OH REACTIONS OF IMPORTANCE IN THE PERTURBED TROPOSPHERE

Progress Report

October 1, 1976

Principal Investigator:

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Project Officer:

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Research Chemist
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U.S. Environmental Protection Agency
Research Triangle Park, North Carolina 27111

During this grant period, rate constants for the reactions of OH radicals with p-xylene, hexafluorobenzene, and n-propyl pentafluorobenzene have been determined using the Flash Photolysis-Resonance Fluorescence technique. The reactions involving p-xylene and n-propyl pentafluorobenzene were carried out at 3 different pressures of helium diluent gas (3, 20, and 200 Torr), while that involving hexafluorobenzene was studied at pressures of 20 and 200 Torr. In addition, during the grant period, measurements on the OH-ethylbenzene system at 3 Torr and the OH-n-propylbenzene system at 20 Torr were also made. We list below these measured rate constants in units of cm^3 $molecule^{-1}s^{-1}$:

(1) OH + p-xylene $\longrightarrow$ Products 300K

3 Torr He $(8.9 \pm .8) \times 10^{-12}$

20 Torr He $(1.13 \pm .10) \times 10^{-11}$

200 Torr He $(1.07 \pm .10) \times 10^{-11}$

(2) OH + hexafluorobenzene $\longrightarrow$ Products 300K

20 Torr He $(2.3 \pm .2) \times 10^{-13}$

200 Torr He $(2.2 \pm .2) \times 10^{-13}$

(3) OH + n-propyl pentafluorobenzene $\longrightarrow$ Products 300K

3 Torr He $(2.5 \pm .2) \times 10^{-12}$

20 Torr He $(3.04 \pm .3) \times 10^{-12}$

200 Torr He $(3.1 \pm .3) \times 10^{-12}$

(4) OH + ethylbenzene $\longrightarrow$ Products 300K

3 Torr He $(7.6 \pm .6) \times 10^{-12}$

20 Torr He $(6.92 \pm .71) \times 10^{-12}$*

200 Torr He $(7.82 \pm .81) \times 10^{-12}$*

(5) OH + n-propylbenzene $\longrightarrow$ Products 300K

20 Torr He $(6.4 \pm .4) \times 10^{-12}$

200 Torr He $(6.22 \pm .81) \times 10^{-12}$*

*These rate constants were measured previous to this grant period.

The rate constant for the reaction of OH with benzene is six times greater than that with hexafluorobenzene. The obvious conclusion is that reduction of electron density on the benzene ring slows down the rate of OH reaction with the aromatic ring. The same trend is noticed when the aromatic ring in n-propylbenzene is fluorinated. The decrease in the rate constant upon the fluorination of the ring is greater than 50%. This result indicates that in n-propylbenzene, abstraction of the benzylic hydrogen by OH is contributing as much as 50% towards the measured bimolecular rate constant. In fact, we propose that this trend holds true for all the mono-substituted benzene compounds. Our results for xylene reactions are easily understood in this scheme of reactivity. The number of benzylic hydrogens in xylene is twice the number in toluene. Furthermore, these extra methyl groups further enhance the electron density on the ring.

These two factors increase the reactivity of xylenes by factors of 2 or 3.

The dislocation of our research group from Maryland took a high toll in terms of time. However, progress is being made in setting up the laser flash photolysis - TOF mass spectrometer system.

10/1/76

AN INVESTIGATION OF OH REACTIONS OF IMPORTANCE IN THE PERTURBED TROPOSPHERE

Progress Report

April 1, 1977

Principal Investigator:

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A. OVERVIEW

During this grant period we have successfully interfaced two different laser systems with a T.O.F. Bendix mass spectrometer. We have initiated two types of studies to elucidate the mechanisms involved in the reactions of hydroxyl radicals with aromatics. The first type of study is being used to identify the products of the reactions in questions; whereas, the second type of study is being employed to quantitatively investigate the formation rates of primary and secondary products. To understand the methodologies involved in each type of study, a brief description of the instrumentation is presented below.

The two basic components in the Georgia Tech system are a T.O.F. mass spectrometer and a high energy pulsed laser. The time-of-flight mass spectrometer (Figure 1) operates by separating, in real time, the ions formed in the ion source into groups characterized by their mass to charge ratio. The ions arrive at the magnetic electron multiplier detector in groups separated in time. This process of ionization, separation, and detection is repeated every 100 μs. Hence, this machine has the potential of acquiring 10,000 mass spectra in one second. There are two methods in which we have operated the T.O.F. during the present investigation: (1) the spectrum acquisition mode and (2) single ion monitoring. In the first mode of operation the output of the magnetic electron multiplier (MEM) is constantly gated into the scope anode--the output of this anode being the mass spectrum. The alter-

native mode of operation is to divert the output of the MEM corresponding to one particular mass into the anode. This provides the abundance of a single ion as a function of time with a time resolution of 100 μs.

The second major component in the G. T. system is the photolysis source. For this function, we are using two different laser systems: (1) a Nd-Yag laser and (2) a tunable dye laser (Figure 2). The fundamental output of the Nd-Yag System (a ILS-NT-572) is quadrupled to give 2650 Å radiation. This wavelength is suitable to photolyze O_3 to give $O(^1D)$, which via the $O(^1D)$-H_2 reaction, is an instantaneous source of OH radicals. Since this first laser system has a repetition rate of 10 pps, substantial concentrations of OH rx products can be built up in a very short period of time (∿ 2 minutes) with a small leak rate from the rx cell. The second laser being used is a tunable dye laser (Phase R) whose output can be doubled to give UV radiation in the spectral region of 2500-3500Å. Single shot outputs from the second system are typically in the 25-100 mJ range.

B. EXPERIMENTAL APPROACH

The basic experimental setup is shown in Figures 3 and 4. In this system, a quartz reaction cell which is equipped with a molecular leak lets a constant fraction of the cell contents effuse into the ionizing region of the T.O.F. mass spectrometer. The mass spectrometer, therefore, is essentially a detector which identifies the constituents and measures the

relative amounts of each species in the effusion mixture. In identifying the reaction products, i.e., the spectrum acquisition mode, the Nd-Yag laser is used to produce hydroxyl radicals through photolysis of O_3, H_2 mixtures. These OH radicals then react with hydrocarbons present in the cell to form products. Since the repetition rate of the Nd-Yag laser is 10 pps, a steady state of chemical reaction and physical effusion is set up, and subsequently the contents of the reaction cell are identified by their mass spec cracking patterns.

In following the time history of a single rx product, the single ion monitoring technique is utilized. Since this experiment needs a higher concentration of the product species, the Phase R tunable dye laser is used. As mentioned earlier, the output of the anode is monitored by feeding an amplified signal into a multi-channel analyzer (MCA). The MCA is triggered to start the ion monitoring by a photodiode which is activated by the photolyzing laser pulse. Thus, the MCA records the intensity of the ion as a function of time. To improve the signal level the data is averaged over many laser shots.

C. RESULTS TO DATE

The T.O.F. mass spec-laser photolysis system, as of this report, has been in operation for only one week; thus, only qualitative results will be reported here. Even so, it is now apparent that this new system, with accompanying fast sampling electronics, represents a major breakthrough in the area of primary

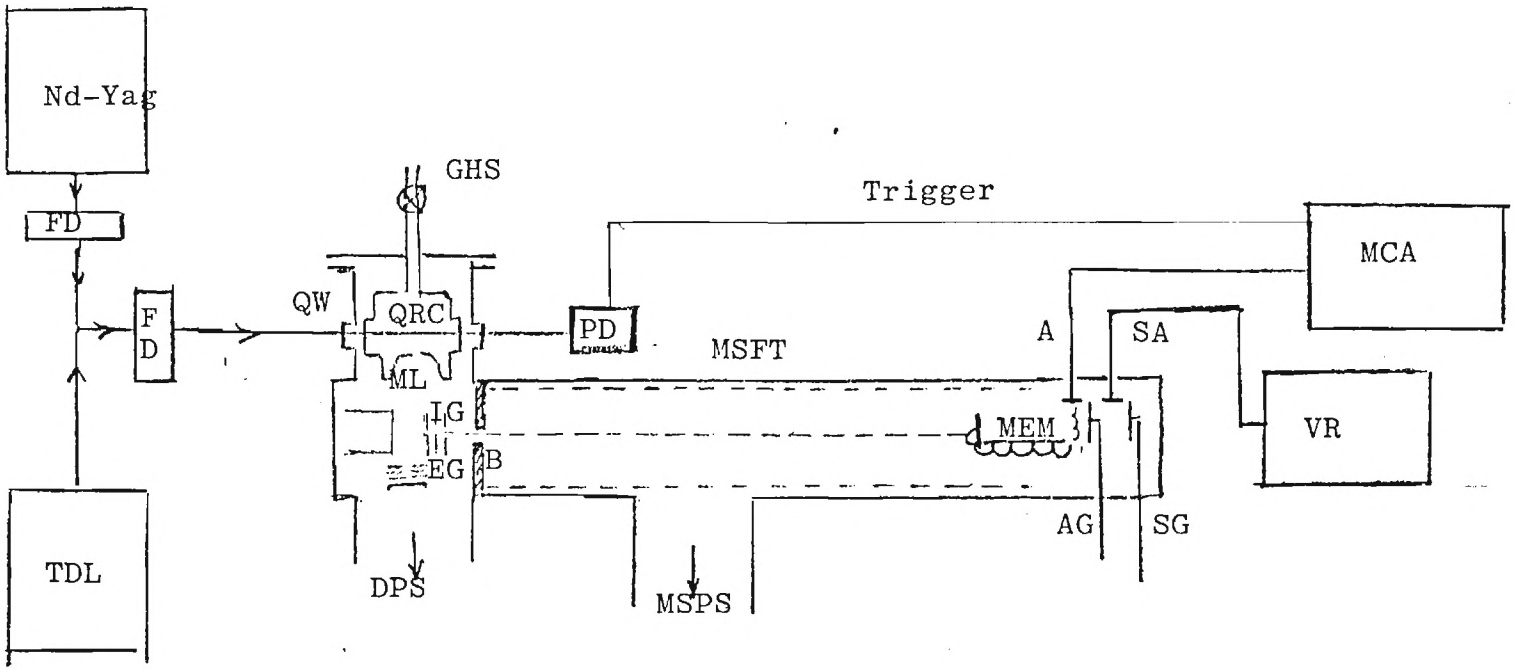
and secondary reaction product analysis. Historically, for complex reaction systems, primary and secondary product yields have had to be inferred from long-time photolysis studies. The T.O.F. mass spec-laser system will now permit an examination of reaction products in the time range of 100 μs to several minutes.

The first reaction system which we have selected to study is that of OH-toluene. Initially, of primary interest to us has been the question of the relative importance of addition versus abstraction in the OH-toluene reaction.* In the latter system, as will be the case for other OH-aromatic rxs, we believe that a very fruitful approach to answering the addition versus abstraction question is that of monitoring the H_2O product from the OH abstraction process. We have now completed our first series of tests on the OH-toluene system and have preliminary results which do indeed show the formation of H_2O on a 100 μs time scale. At the present time, however, the system has not been optimized for this experiment. By further increasing the laser energy by a factor of five and using a quartz reaction cell with a much smaller molecular leak (i.e., 20 μ versus 100μ) an increase in our present signal of $\sim$ 10 can be expected. The smaller leak will also permit higher total pressures in the reaction cell (i.e., 100 Torr vs 3 Torr), thus permitting a more realistic appraisal of the abstraction versus addition modes.

*See our Progress Report for the first quarter of the grant period.

The second phase of our newly initiated study in OH-aromatic reaction kinetics will involve the analysis of the OH-aromatic adduct or ring fragmentation products. Qualitative experiments are now under way to achieve this objective in the OH-toluene system.

Looking still further ahead, we intend soon to substitute H_2O_2 for O_3-H_2 mixtures as the source of OH radicals. Planned improvements in both the laser intensity and the sensitivity of the T.O.F. mass spec should make this possible within a few months.



TDL - Tunable Dye Laser
FD - Frequency Doubling Crystal
Nd-Yag - Neodymium-Yag Laser
GHS - Gas Handling System
QRC - Quartz Reaction Cell
QW - Quartz Window
ML - Molecular leak
EG - Electron Grids
IG - Ion Grid
DPS - Differential Pumping Station

MSFT - Mass Spec Flight Tube
MSPS - Mass Spec Pumping Station
P.D. - Photo-diode
B - Baffle
MEM - Magnetic Electron Multiplier
A - Anode
AG - Anode Gate
SA- Scope Anode
SG - Scope Gate
VR - Visicorder- Recorder
MCA - Multichannel Analyzer

Figure 4. A Schematic Drawing of the Laser Photolysis- TOF Mass Spectrometer System

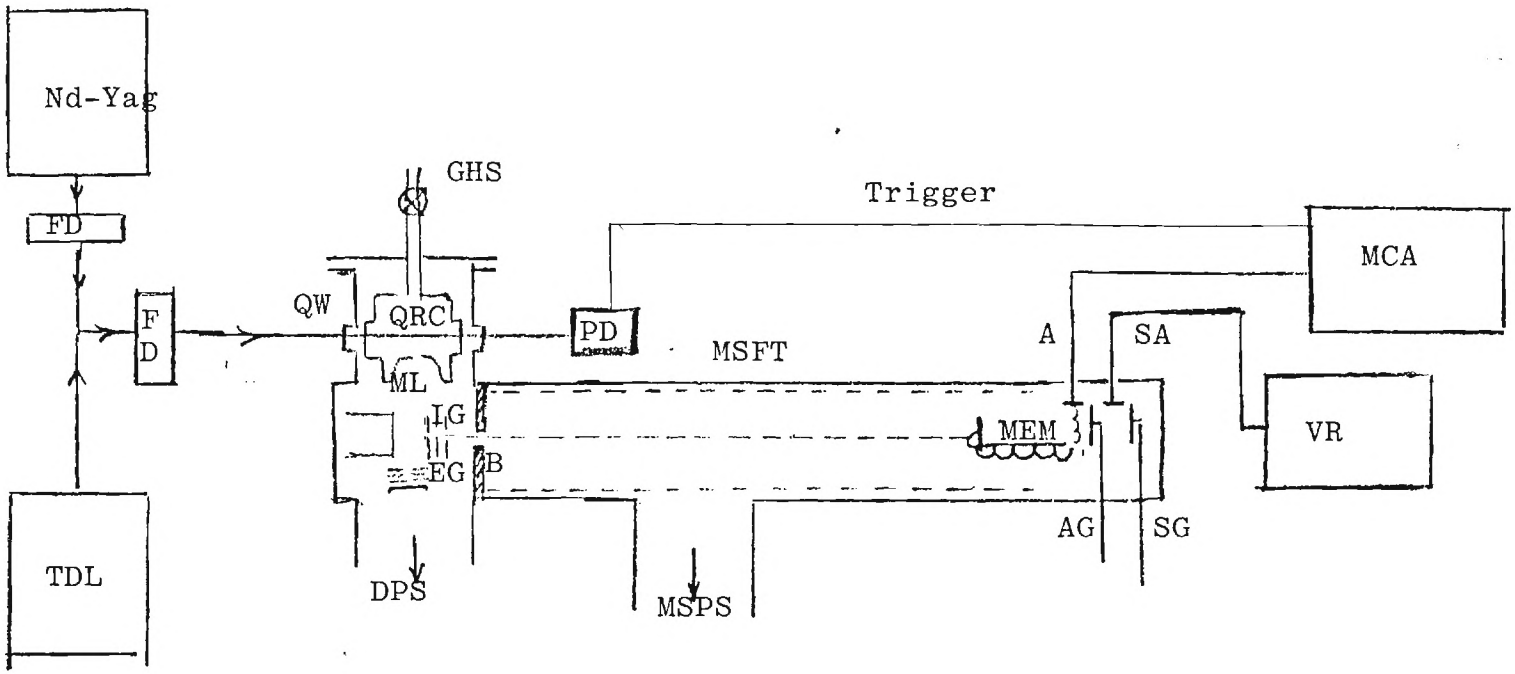


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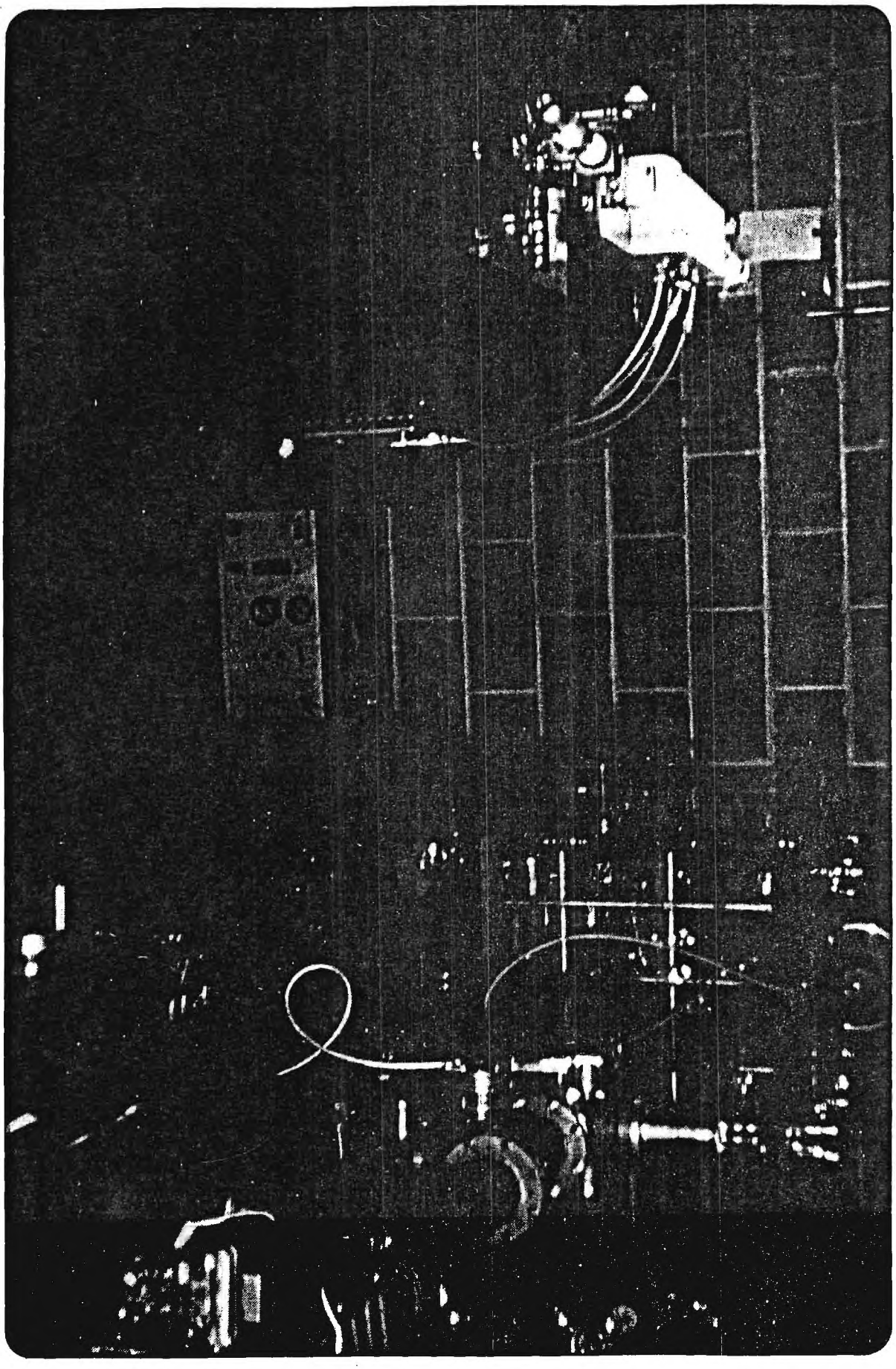
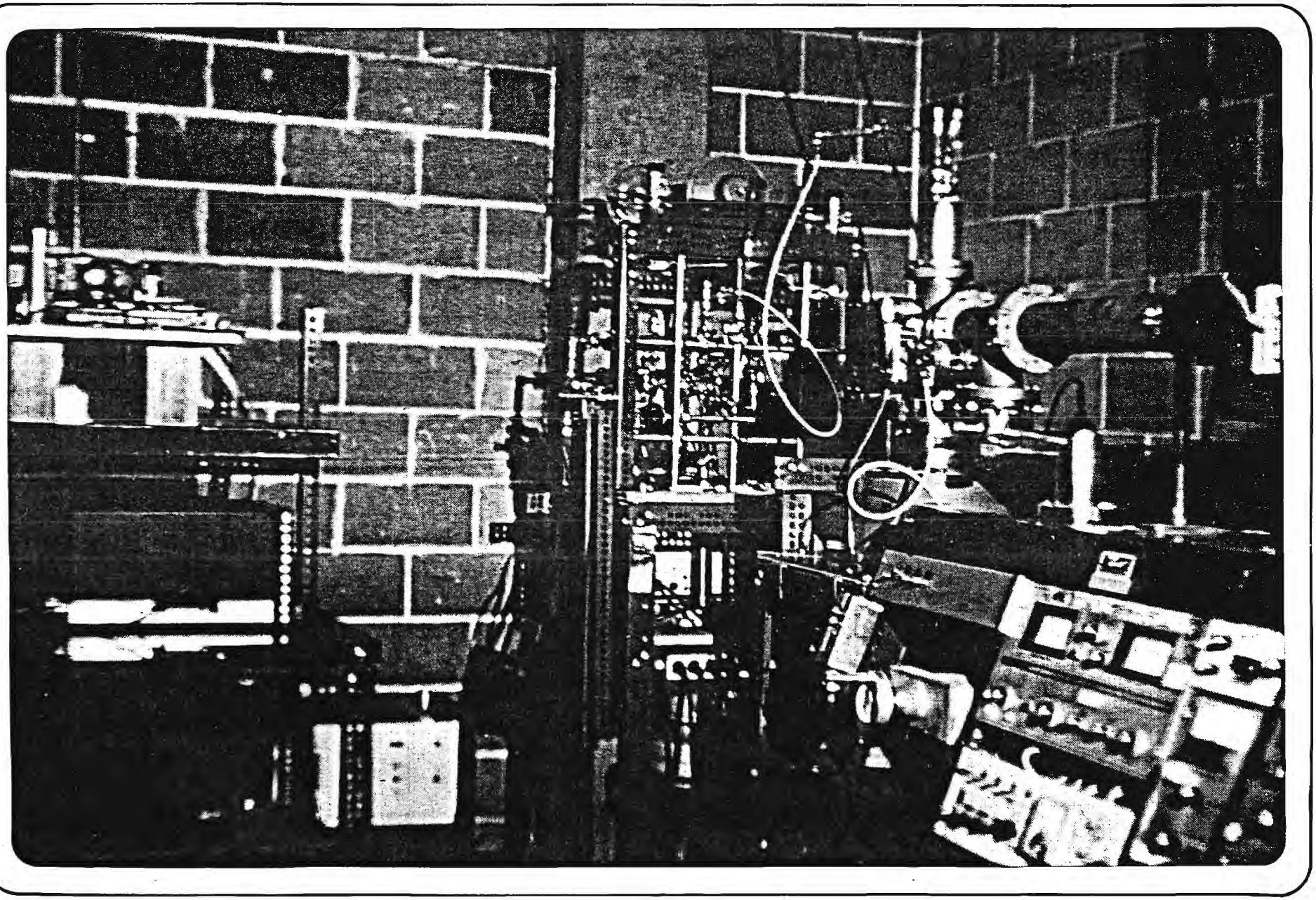
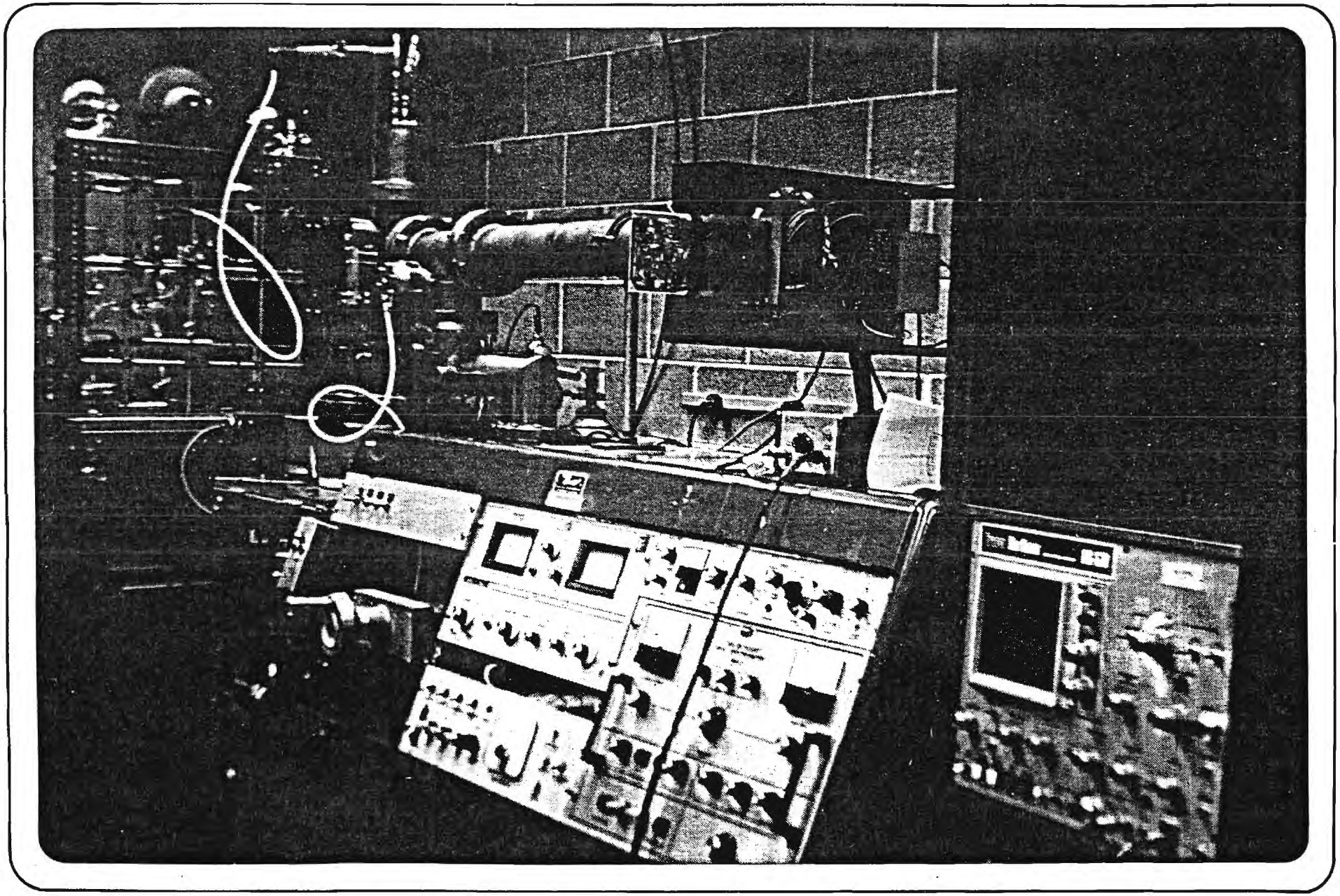
Figure 4. A Schematic Drawing of the Laser Photolysis- TOF Mass Spectrometer System







B-423

AN INVESTIGATION OF OH REACTIONS OF IMPORTANCE IN THE PERTURBED TROPOSPHERE

by

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ABSTRACT

The flash-photolysis resonance fluorescence technique has been utilized to study the reaction kinetics of hydroxyl radicals with ten aromatic and six olefinic hydrocarbons at 298 K and several diluent gas pressures. The aromatic compounds that were studied include benzene, toluene, ethylbenzene, n-propylbenzene, isopropylbenzene, hexafluorobenzene, n-propyl pentafluorobenzene, and o-, m-, and p-xylenes; and the olefins include ethylene, acetylene, propylene, 1-butene, cis-2-butene, and tetramethylethylene. Based on our extensive data on OH-substituted aromatic hydrocarbon reactions, it has been inferred that addition of hydroxyl radicals to the aromatic ring is the dominant reaction in these systems.In the case of OH-olefin reactions,addition of OH to the double bond seems to be a prominent path for the heavier unsaturates. From these rate constant data the lifetimes of all these hydrocarbons in the lower troposphere has been calculated. Utilizing the technique of laser flash photolysis, time-of-flight mass spectrometry, attempts were made to understand the mechanisms involved in the reactions of OH with substituted aromatic hydrocarbons.

CONTENTS

FIGURES

TABLES

TABLES (Continued)

SECTION 1

AN INVESTIGATION OF OH REACTIONS OF IMPORTANCE IN THE PERTURBED TROPOSPHERE

In the last ten years, atmospheric chemistry has increased in both breadth and significance. During this time period, there has been a growing sense of awareness on the part of the scientific community and the general public that our plant's atmosphere, for all its enormity, is still rather fragile. The atmosphere is not a passive reservoir, capable of storing endless amounts of waste products from increasing industrialization. Trace gases and aerosols injected into the atmosphere by man interact chemically and physically with natural constituents. Some toxic species are produced; some essential or productive species are depleted; and the concentrations of those trace constituents which are primarily responsible for maintaining the radiative and precipitation budgets of the atmosphere are being altered.

A complex web of competing and successive photochemical, free radical, and molecular reaction rates determine, in combination with poorly understood molecular diffusion considerations, the nature of the atmosphere. An assessment of the rates of formation or degradation of atmospheric species necessitates a knowledge of the molecular concentrations, reaction rate constants, and mechanisms of reaction of processes involving both the species of interest and all influencing sources and sinks.

Hydroxyl radical reactions are among the most important laboratory

studies presently being conducted in atmospheric chemistry. Among the key processes now receiving considerable attention are those involving the reactions of hydroxyl radicals with organic pollutants. The extremely reactive OH radical is thought to be the principal means of removal for most airborne toxic chemicals (some undoubtedly carcinogenic) released by a wide assortment of man's industrial activities.

The spectrum of organic pollutants of interest here includes: chemical industry solvents, such as benzene, toluene, tetrahydrofuran, xylenes, etc.; chlorinated solvents used in metal-working plants, dry cleaning processes and paints; and saturated and unsaturated hydrocarbons emitted from internal combustion engines. The photochemical smog cycle is, in fact, a special case within a localized air mass of the degradation cycle described above. Thus, our efforts which have been directed towards obtaining rate constants and investigating the mechanisms of the OH-hydrocarbon reactions has local, regional, and global importance in terms of air management.

We have described in the following sections the results of our investigations on OH-hydrocarbon reactions. They are:

Section 2: "A Kinetics Study of the Reaction of the OH Free Radical with Aromatic Compounds. 1. Absolute Rate Constants for Reaction with Benzene and Toluene at 300°K"

Section 3: "A Kinetics Study of the Reaction of OH Radicals with Two C_2 Hydrocarbons: C_2H_4 and C_2H_2"

Section 4: "A Kinetics Study of the Reaction of OH Radicals with Aromatics and Olefins"

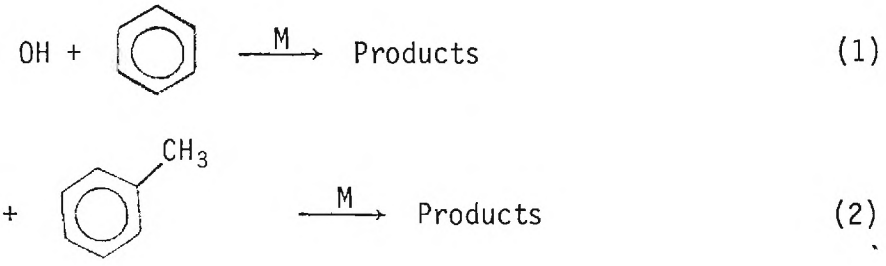
Section 5: "Identification of OH-Hydrocarbon Reaction Products"

SECTION 2

A KINETICS STUDY OF THE REACTION OF THE OH FREE RADICAL WITH AROMATIC COMPOUNDS. 1. ABSOLUTE RATE CONSTANTS FOR REACTION WITH BENZENE AND TOLUENE AT 300°K

INTRODUCTION

Whereas considerable work has been reported on the reaction of OH with paraffinic and olefinic hydrocarbons,[1-8] virtually no systematic study has been carried out on aromatics. We wish to report, therefore, a recent study completed in our laboratory involving the reaction of OH with two aromatic compounds, benzene and toluene.



To the best of our knowledge, the absolute rate constants given represent the first absolute rate constants reported for these organic species. The importance of these new measurements (in addition to their obvious fundamental significance to kinetics) lies in the fact that OH-aromatic reactions are of major concern in the combustion of nonleaded gasoline and in the formation of photochemical smog. For example, recent examinations of the emissions from cars running on regular nonleaded gasoline have shown that over 20% of the hydrocarbons emitted were aromatics.[9]

EXPERIMENTAL SECTION

In this study the reaction of OH with benzene and toluene was followed by monitoring the concentration of OH as a function of time. The detection technique for OH was that of resonance fluorescence which has been discussed in detail in previous publications.[10,11] The photolysis of H_2O (in the region above the CaF_2 cut off at 1250 Å) as a source of OH has also been described in earlier work.[11]

In all experiments reported here, gas mixtures were made up using an all-glass gas handling system. The toluene and benzene used in this study were from Fischer Scientific Co. and had a purity level of 99.96% or better. All low-pressure measurements of toluene, benzene, and H_2O were made using a MKS Baratron. High-pressure measurements (10-800 Torr) were made with a two-turn Bourdon gauge (Wallace and Tiernan Type FA145). The precision to which gas mixtures could be prepared, with the exception of H_2O, was estimated to be ∿3% or better.

RESULTS AND DISCUSSION

The results from experiments performed at various total heliem pressures are shown in Tables I and II. Of considerable interest here is the observed pressure dependence for the reaction of OH with both benzene and toluene; also there is the fact that for both compounds rather large k values were measured at 100 Torr He pressure, $k_1 = 1.59 \pm 0.12 \times 10^{-12}$ and $k_2 = 6.11 \pm 0.40 \times 10^{-12}$ cm^3 $molecule^{-1}$ sec^{-1}. In each case, the bimolecular rate constants reported were obtained from the slope of a plot of the pseudo-first order rate constant k vs. the aromatic concentration. The nonzero value for k at zero reactant pressure represents the loss rate of OH due to diffusion out of the sampling region.[10,11] A close examination of the pressure dependence shown in Tables I and II for benzene and toluene indicates that over the pressure range studied in this work the reported rate constants are in the pressure fall off region for each reaction (e.g., the rate constant is not a true third-order rate constant nor is it a true bimolecular rate). The rate constant reported, therefore, is calculated in the form of a bimolecular rate constant at each total gas pressure employed. To better estimate the high-pressure limiting k value for these processes, a Lindemann plot (1/k vs. 1/p) is given for both aromatics in Figure 1. This figure clearly shows that benzene has a greater pressure dependency than toluene as might be expected; but, somewhat surprisingly, it also indicates that a very significant fraction of the total reaction of toluene with OH proceeds by the addition of OH to the aromatic ring. The evidence here is the fact that the change in the effective

TABLE I. Rate Data for the Reaction of OH with Benzene at 298°K[a]

[Reactant] m Torr	[Diluent] Torr	Flash Energy, J	k', s^{-1}	k_{bi}, cm^3 $molecule^{-1}$ s^{-1}
0	3 (He)	88	210	
2	3	88	267	
4	3	88	322	
8	3	88	430	$(0.849 \pm 0.08) \times 10^{-12}$
0	20 (He)	88	68	
0.5	20	88	87	
3	20	88	205	
5	20	88	295	
5	20	88[b]	330	
5	20	45	290	
5	20	180	330	
8	20	88	420	$(1.36 \pm 0.09) \times 10^{-12}$
0	100 (He)	88	36	
3	100	88	190	
6	100	88[c]	350	
9	100	88	500	$(1.59 \pm 0.12) \times 10^{-12}$

[a] In all experiments, CaF_2 window was used and the pressure of H_2O, the photolyte, was 100 m Torr.
[b] 150 flashes/gas filling (for all other experiments only 30 flashes/filling was used).
[c] 200 m Torr of H_2O

TABLE II. Rate Data for the Reaction of OH with Toluene at 298°K[a]

[Reactant] m Torr	[Diluent] Torr	Flash Energy,J	k',s^{-1}	k_{bi}, cm^3 $molecule^{-1}$ s^{-1}
0	3 (He)	88	210	
1	3	88	325	
1.5	3	88	390	
2	3	88	450	
3	3	88	565	$(3.60 \pm 0.26) \times 10^{-12}$
0	20 (He)	88	68	
0.5	20	88	170	
1	20	88	240	
1.5	20	88	330	
1.5	20	88[b]	310	
1.5	20	45	290	
1.5	20	180	350	
2	20	88	390	
3	20	88	555	
4.5	20	88	790	$(5.00 \pm 0.18) \times 10^{-12}$
0	100 (He)	88	36	
1	100	88	250	
2	100	88	425	
3	100	88	630	$(6.11 \pm 0.40) \times 10^{-12}$

[a,b]See corresponding footnotes to Table I.

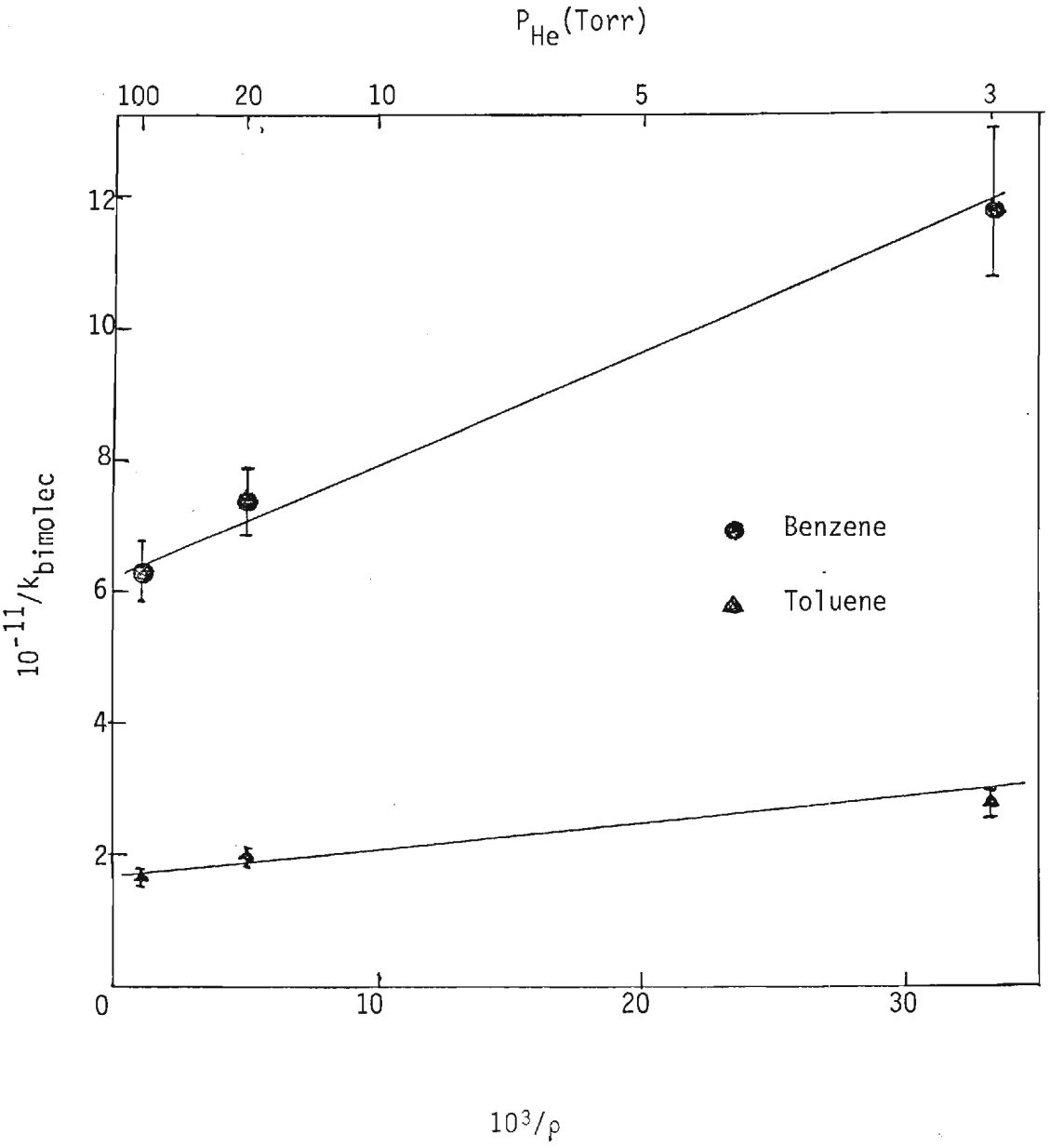


Figure 1. A 1/k vs. 1/p Lindemann plot showing the pressure dependence of the reaction of OH with benzene and toluene.

bimolecular rate constant from 3 Torr to 100 Torr is nearly a factor of 2. Since only the addition reaction would show a pressure dependence, it is concluded that at least half of the total reaction is additions. Because of the weak benzyl carbon-hydrogen bond in toluene it is to be expected that some abstraction is also occurring although our data only indicate that the importance of this process is probably less than 50% of the total reaction. The dependence of the bimolecular rate constant on the total pressure for both reactions (1) and (2) can be explained on the basis of OH adding directly to the aromatic ring. A possible explanation for the observed difference in the pressure dependency for the two reactions is the larger number of degrees of freedom available in the case of toluene for stabilization of the transition complex. Figure 1 also indicates that toluene is more reactive than benzene by at least a factor of 4. This can be explained by the higher efficiency of the addition process for reaction (2), but also important, as indicated above, is the fact that reaction (2) can proceed by abstraction as well as by addition. The second process would involve abstracting a hydrogen atom from the methyl group on toluene.

There has been much speculation as to whether OH only abstracts the α hydrogens of branched aromatics or whether addition to the ring in possible. This study indicates that the addition process is very important for toluene and will therefore have a very significant effect on the product distribution resulting from reaction (2).

Concerning the possible role of aromatics in smog formation, an examination of Figure 1 would indicate that at near atomospheric pressure (for the case of M = He) the respective rate constants for processes 1 and 2 would probably be very close to their 100 Torr values, 1.59×10^{-12} and 6.11×10^{-12}

cm^3 $molecule^{-1}$ sec^{-1}. Using an estimated OH steady-state concentration for the atmosphere of 5×10^6 molecules/cc would therefore give a 1/e lifetime for benzene and toluene of $\sim$36 and 10 hr under daylight conditions. (This would probably be even shorter if rate constants for M = N_2 were to be used.) From these simple calculations, along with available concentration data, aromatic compounds would now appear to contribute to the formation of photochemical smog in areas involving heavy automobile traffic.

SECTION 3

A KINETICS STUDY OF THE REACTION OF OH RADICALS WITH TWO C_2 HYDROCARBONS: C_2H_4 AND C_2H_2

INTRODUCTION

Hydroxyl radical reactions have been the subject of considerable interest in recent years due to their importance in combustion processes and in the chemistry of the atmosphere. Ethylene is thought to be a minor, but significant constituent of the effluents emitted from automobile exhausts,[12] and its presence in urban atmospheres has been shown to increase the rate of conversion of NO to NO_2, which is the precursor for the formation of ozone.[13] The reaction of hydroxyl radicals with ethylene is now thought to be an important step in this process.

$$C_2H_4 + OH \longrightarrow \text{Products (e.g., } C_2H_5O) \text{ .} \qquad (1)$$

The reaction of hydroxyl radicals with acetylene is of importance in the degradation of acetylene to CO_2, both in the atmosphere and in diffusion controlled flames.

$$C_2H_2 + OH \longrightarrow \text{Products (e.g., } C_2H_2O + OH) \text{ .} \qquad (2)$$

As a result of the importance of reactions (1) and (2) there have been numerous studies of these chemical systems.[3-5,14-18] In the case of reaction (1), the values reported by different workers for the rate constant at ambient temperatures ($\sim 300^{\circ}K$) are at variance by as much as a factor of 3.[3-5,14-16] Most of these previous studies, which were performed in both flow and static

systems using a wide variety of detection techniques, were carried out at total pressures lower than 20 Torr. In none of these investigations was a systematic variation in pressure performed.

Morris, et al.[3] qualitatively observed mass spectrometric adduct peaks in their study of reaction (1), and proposed the primary process to be

$$OH + C_2H_4 \longrightarrow C_2H_5O \ . \qquad (1a)$$

Bradley, et al.[5] also reported observing the adduct peak, but in addition observed peaks indicating that ethanol also plays a role in the overall mechanism.

Of the studies on reaction (2) documented in the literature, only four were performed at room temperature[15-18]; and the rate constants reported varied by as much as a factor of 5. Those studies carried out in flow systems[16-18] used low initial stoichiometries ($[C_2H_2]_0/[OH]_0$, ranging from (2.3 to 120), which resulted in stoichiometric corrections being required for most of the rate constant data. However, only one study[17] actually measured the stoichiometric correction factor, n, while other workers reported either k_2/n or used the single value of n which had been previously published. A more recent study performed,[15] using the flash-photolysis resonance absorption technique, employed moderately high initial stoichiometries, e.g., $[C_2H_2]_0/[OH]_0 \sim 10^2$. That study reported that corrections to the rate data due to secondary processes were not required.

Breen and Glass[17] used mass spectrometric product analysis to obtain a value for the stoichiometry of reaction (2). From this it was argued that the following two channels were consistent with the data:

$$OH + C_2H_2 \longrightarrow C_2HO + H_2 \qquad (2a)$$

$$OH + C_2H_2 \longrightarrow C_2H + H_2O\ , \qquad (2b)$$

while the following was not:

$$OH + C_2H_2 \longrightarrow CH_3 + CO\ . \qquad (2c)$$

However, evidence obtained from a crossed molecular beam experiment (Gehring, et al.)[19] supported reaction (2c) as being the dominant primary process. Kanofsky, et al.,[20] on the other hand, proposed that the primary process was not (2a), (2b), or (2c), but rather

$$OH + C_2H_2 \longrightarrow C_2H_2O + H\ . \qquad (2d)$$

EXPERIMENTAL SECTION

The flash photolysis-resonance fluorescence technique has been described in great detail in previous publications[11,21] and only a summary description will therefore be presented in this text.

As in an earlier study involving reactions of the hydroxyl radical,[11,21] photolysis of H_2O was used as the source of OH:

$$H_2O + h\nu \xrightarrow{\lambda>140nm} H + OH\ (X^2\Pi)\ .$$

In the present study, reaction mixtures consisted of 50-300 mTorr of H_2O, 20-500 Torr of He, and either 1-7 mTorr of C_2H_4 or 2-30 mTorr of C_2H_2. These mixtures were photolyzed using a N_2 spark flash lamp equipped with either a CaF_2 or Suprasil quartz window. CaF_2 was used in the study of reaction (1) almost exclusively to reduce the photolysis of C_2H_4. Similarly in the case of reaction (2), Suprasil windows were normally used to minimize photolysis of C_2H_2. Based upon the known absorption spectrum of H_2O and previously conducted actinometry on the flash lamp using ethylene as the actinic gas, it was determined that within the spectral range 105-200 nm on the order of $1.5\text{-}36 \times 10^{11}$ OH radicals/cm^3 were typically produced per flash in the reaction cell (the precise flash energy, the spectral bandwidth, and the H_2O concentration defined the actual concentration).

Excitation of OH was accomplished via the use of an OH resonance lamp. This lamp primarily produced the emission characteristic of the $(A\Sigma^{2+}:v'=0) \rightarrow (X^2\Pi:v''=0)$ transition of OH. A small fraction of the OH, produced by the

photolysis of H_2O, was continuously excited by the emission from this lamp. Fluorescence from excited OH was measured using a photomultiplier tube located at right angles to the lamp. The intensity of this fluorescent emission was found to be directly proportional to the amount of OH present in the mixture. The fluorescence signal from the photomultiplier tube was then stored as a function of time in a multichannel analyzer, operated in the multiscaling mode.

Since the C_2H_4 and C_2H_2 pressures were adjusted to make reactions (1) and (2) kinetically pseudo-first order with respect to OH, the observed rate of OH disappearance was always exponential. Because the OH concentrations utilized in the two studies was low ($[OH]_0 \leq 3.6 \times 10^{12}$ molecule cm^{-3}), the observed signal levels were also low. Thus, multiple flashes on a single gas mixture were required to produce a single smooth kinetic decay curve. However, the number of flashes per gas mixture was always restricted to minimize the decomposition of C_2H_2 or C_2H_4 to less than 3%. Thus, several fillings of an identical gas mixture were used for the development of a single experimental decay curve. The initial hydroxyl radical concentration was kept low in order to ensure that the bimolecular disproportionation reaction of hydroxyl radicals could be neglected, and to obtain high initial stoichiometries, typically ($[C_2H_2]_0/[OH]_0 \geq 500$), so that the importance of secondary reactions could be minimized. Even with high initial stoichiometries, however, secondary reactions were not always eliminated (to be discussed later).

Since the observed kinetics were pseudo-first order, the first order rate constants could be obtained from a plot of the logarithm of the count rate in each channel of the analyzer (after the background was subtracted) versus time. The slope of the line in each case was established by a least

squares treatment of the data. This treatment was extended out to two and in some cases three 1/e times of the decay. Bimolecular rate constants were obtained from a least squares treatment of the slope of the line obtained from a plot of the pseudo-first order rate constants versus C_2H_2 or C_2H_4 pressure. Each bimolecular rate constant, therefore, represents an average of more than ten individual experiments.

Gas pressures of less than 3 Torr were measured using an MKS Baratron pressure gauge which was periodically checked against a dibutyl phthalate manometer. The high pressure measurements (10-800 Torr) were made with a two-turn Bourdon gauge (Wallace and Tierman type FA-145). The precision to which gas mixtures could be made, with the exception of H_2O, was estimated to be 3% or better. The H_2O pressure could not be metered so precisely due to adsorption effects on the surfaces of the reaction cell.

The C_2H_2 and C_2H_4 used in these experiments were from Matheson Co. and had stated purities of 99.6% and 99.98%. Both gases were degassed in liquid nitrogen prior to use. Matheson "Gold Label Ultra-High Purity" helium was used without further purification. The H_2O used in all experiments was distilled and then degassed using liquid N_2 prior to its introduction into the gas handling system.

RESULTS AND DISCUSSION

A. $OH + C_2H_4 \longrightarrow$ Products

The results for reaction (1) are presented in Table I. It can be seen that a wide variation in experimental conditions was performed in an effort to show that kinetic complications were not affecting the observed rate constants. These variations included using H_2O pressures of 50 to 300 m Torr, flash energies of 45-$\sim$500 J, and ethylene pressures of 1-7 m Torr. Under these widely differing conditions the pseudo-first order rate constants were found to be invariant (for any given C_2H_4 pressure) within the assigned experimental uncertainties of the measurements. The indications are, therefore, that OH reactions of the following type were not significant:

$$C_2H_4 + h\nu \longrightarrow \text{fragments}, \quad (3)$$

$$OH + \text{fragments} \longrightarrow \text{products}, \quad (4)$$

$$OH + OH + M \longrightarrow H_2O_2 + M, \quad (5)$$

$$OH + OH \longrightarrow H_2O + O, \quad (6)$$

$$H + OH + M \longrightarrow H_2O + M, \quad (7)$$

$$O + OH \longrightarrow O_2 + H. \quad (8)$$

In addition, the reaction of OH with the products of (1) could not be important. In all the above cases, the rate of removal of OH would depend upon the square power of the flash intensity since the radical concentration in these rate expressions depends directly upon the flash energy. If these reactions had been significant, then there would have been an observed

TABLE I. Rate Data for the Reaction of OH with Ethylene at 298°K

[Reactant] m Torr	[Diluent] Torr	Flash Energy, J	k', s^{-1}	k_{bi}, cm^3 $molecule^{-1}$ s^{-1}
0	3 (N_2)	320	83	
1	3	320	220	
2	3	500	325	
3	3	500	420	$(3.64 \pm 0.20) \times 10^{-12}$
0	3 (He)	88	205	
1	3	88	290	
1	3	500	295	
2	3	88	370	
2	3	500	365	
3	3	500	430	
5	3	88	525	
5	3	500	575	$(2.24 \pm 0.22) \times 10^{-12}$
0	5 (He)	88	140	
5	5	320	585	$(2.79 \pm 0.37) \times 10^{-12}$
0	6 (He)	88	120	
1	6	88	230	
2	6	88	330	
3	6	88	445	$(3.32 \pm 0.43) \times 10^{-12}$
0	10 (He)	88	105	
2	10	88	340	$(3.63 \pm 0.50) \times 10^{-12}$
0	20 (He)	88	70	
1	20	88	215	
2	20	45	350	
2	20	88	365	
2	20	500	380	
3	20	88	500	
5	20	88	700	$(4.06 \pm 0.38) \times 10^{-12}$

TABLE I. (Continued)

[Reactant] m Torr	[Diluent] Torr	Flash Energy,J	k',s^{-1}	k_{bi}, cm^3 $molecule^{-1}$ s^{-1}
0	100 (He)	88	40	
1	100	88	204	
2	100	88	350	
3	100	88	510	
5	100	320	650	$(4.72 \pm 0.60) \times 10^{-12}$
0	300 (He)	88	28	
0.5	300	88	140	
1	300	88	210	
1.5	300	88	267	
2	300	88	362	$(5.33 \pm 0.65) \times 10^{-12}$

The pressure of H_2O, the photolyte, was 100 m Torr.

dependence of k_1 upon the flash intensity. Finally, since the products of ethylene photolysis consist chiefly of H_2 and C_2H_2,[22,23] experiments were performed in which the number of flashes per gas filling was varied. The range of this variation was 10 to 100. Reactions of possible importance here would include the following:

$$OH + H_2 \longrightarrow H_2O + H \quad (9)$$

$$OH + C_2H_2 \longrightarrow \text{products}. \quad (2)$$

The results of this test were that within the experimental error of the measurements (±6%) no variation in the observed first-order rate constants was noted. Even though secondary reactions (2)-(8) were found to be insignificant under our experimental conditions, a CaF_2 window (λ>120 nm) was used over the flash lamp to limit the extent to which C_2H_4 was photolyzed.

A possible source of systematic error in the above measurements could involve rotationally or vibrationally excited OH species produced by the flash pulse. Previous experiments[11,21] utilizing 307 nm and 345 nm interference filters over the resonance lamps indicated that vibrationally excited OH, if present, was not directly detected by the system. If there was a significant initial population of OH in the v''=1 level, which was subsequently quenched into the v''=0 level, then an apparent underestimate in the pseudo-first order rate constants would be noted due to the slow production of ground state OH. However, previous experiments[11,21] utilizing 40 m Torr of CO, 20-100 Torr of He or 20 Torr of N_2, and 50-300 m Torr of H_2O for the study of reaction (10)

$$OH + CO \longrightarrow CO_2 + H \quad (10)$$

showed no evidence for quenching of excited OH outside of the experimental uncertainty. If there had been a significant population of excited OH, then

the observed rate constant would have varied with total pressure due to quenching, and the decay plots would not be logarithmic as observed. Thus, at the pressures utilized in this study, excited OH does not appear to have been a problem in defining a value for either k_1 or k_2.

The only experimental parameter which caused deviations in k_1 outside the experimental uncertainty were variations in total pressure. Within the experimental range of pressure 3-300 Torr of He, a variation of a factor of 3 in the experimentally determined value of k_1 was observed. Experiments utilizing 3 Torr of N_2 were also performed. The He pressure data are presented in Figure 1 as the logarithm of the bimolecular rate constant versus the logarithm of the total pressure. The observed results indicate that reaction (1) is intermediate between second and third order in the pressure range examined in this study.

The present results indicate that within the pressure range 3-300 Torr of He, the bimolecular rate constant varies from 2.24 to 5.33 x 10^{-12} cm^3 $molecule^{-1}$ s^{-1}. The estimated uncertainty in all first-order rate constants was judged to be ±6%. The uncertainties in the bimolecular rate constants represent two standard deviations of the mean, as determined from a linear least-squares-curve fitting technique. In general, these uncertainties ranged in value from 10 to 13%.

B. $OH + C_2H_2 \longrightarrow$ Products

Table II summarizes the data used to compute the bimolecular rate constant for reaction (2) at 300°K. As in the case of reaction (1), wide variations in experimental conditions were performed. The H_2O pressure was reduced from 300 m Torr by a factor of 6, the total pressure (He) was varied

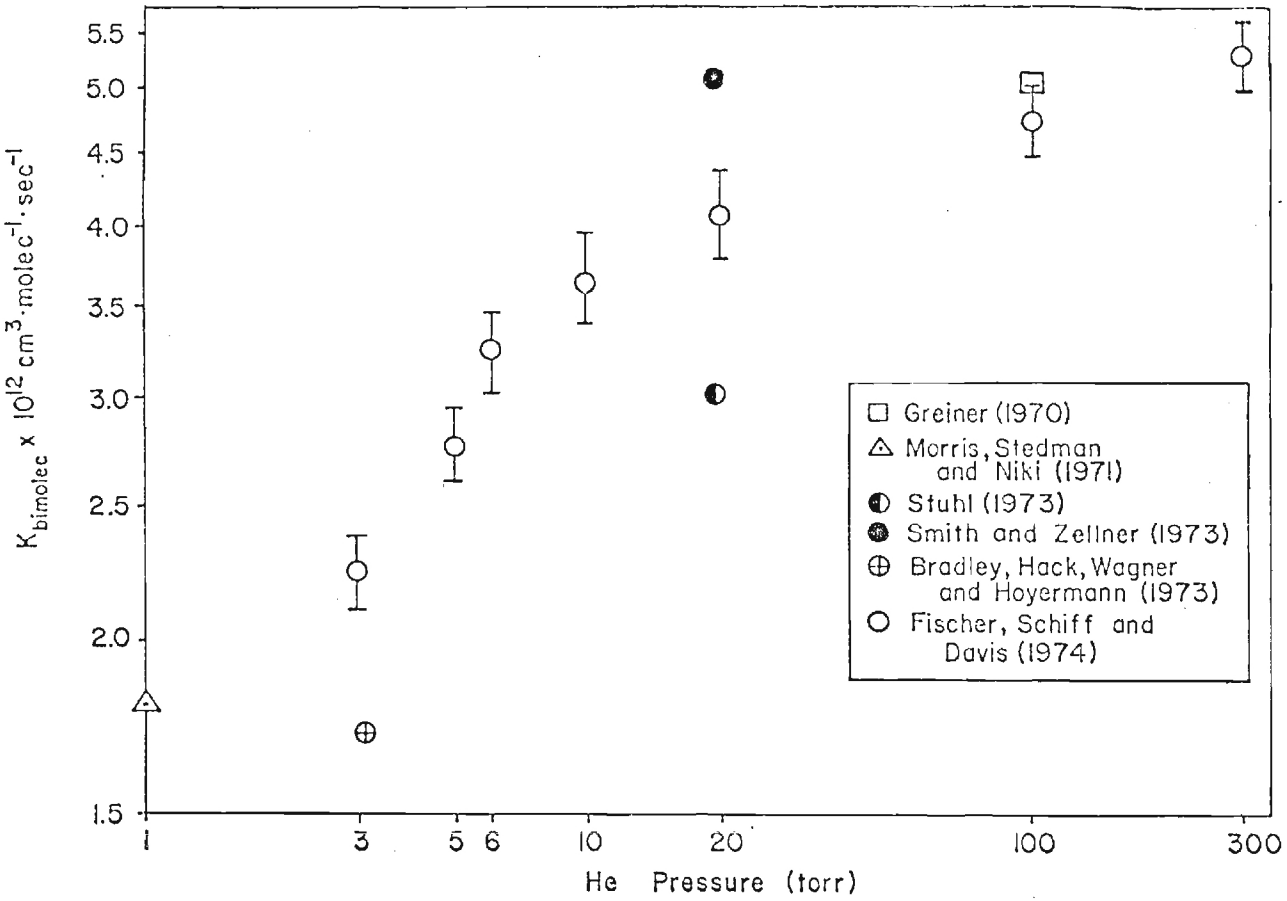


Figure 1. A plot of log k_2 (the bimolecular rate constant) vs. log P(He) for the reaction of OH with ethylene.

TABLE II. Rate Data for the Reaction of OH with Acetylene at 298°K

[Reactant] m Torr	[Diluent] Torr	H_2O m Torr	Flash Energy, J	k', s^{-1}	k_{bi}, cm^3 $molecule^{-1}$ s^{-1}
0	20 (He)	100	88	45	
2	20	100	88	58	
10	20	100	88	105	
10	20	100	88	97	
10	20	100	45	103	
20	20	100	88	155	
20	20	150	88	155	
20	20	150	88	160	
30	20	150	88	205	$(1.68 \pm 0.12) \times 10^{-13}$
0	50 (He)	300	45	43	
5	50	300	45	69	
10	50	300	45	99	
15	50	300	45	125	$(1.73 \pm 0.13) \times 10^{-13}$
0	100 (He)	300	88	25	
2	100	300	45	33	
5	100	300	20	45	
5	100	300	45	48	
10	100	300	20	72	
10	100	50	45	76	
20	100	300	20	135	
20	100	300	45	125	
20	100	300	320	225	
20	100	300	500	340	
30	100	300	45	185	$(1.61 \pm 0.17) \times 10^{-13}$
0	500 (He)	300	45	22	
5	500	300	45	48	
10	500	300	20	72	
10	500	300	45	71	$(1.55 \pm 0.18) \times 10^{-13}$

by a factor of 25 (20-500 Torr), and the acetylene pressure ranged from 2 to 30 m Torr. For a constant acetylene pressure, no significant variations of the pseudo-first order rate constant outside of the experimental error were observed for the above changes. Variation of the flash intensity by a factor of ∿25 (20-∿500 J) did show significant perturbations in the first-order rate constants.

Figure 2 shows the variation in the pseudo-first order rate constant as a function of acetylene pressure for several flash energies. The dependence of the pseudo-first order rate constant with flash intensity was thoroughly investigated at a fixed total pressure (100 Torr) and fixed acetylene pressure (20 m Torr). For flash energies of 320 J the observed first order rate constants were nearly a factor of 2 faster than those obtained at energies ≤45 J. The data collected using flash energies >45 J were prone to scatter and the individual logarithmic decay plots were not always strictly linear, indicating the importance of secondary processes. These high flash energy experiments were particularly sensitive to changes in the transmission characteristics of the flash lamp window, as this governed the photon flux entering the cell. Changes in transmission properties were due to material being deposited upon the window from the electrodes, and to F-center formation in the window. When the flash energy was varied below 88 J there was no perceptible deviation in the observed rate constants outside of the bounds of the experimental error.

There are numerous possible explanations for the above observations, some of which will now be explored in greater detail. The experimental data suggest that the flash decomposition product of acetylene, C_2H, should not be important as its concentration can be calculated to be $\sim \frac{1}{30} [OH]_0$ (this is based upon the relevant absorption cross-section data of H_2O [24] and C_2H_2,[25,26]

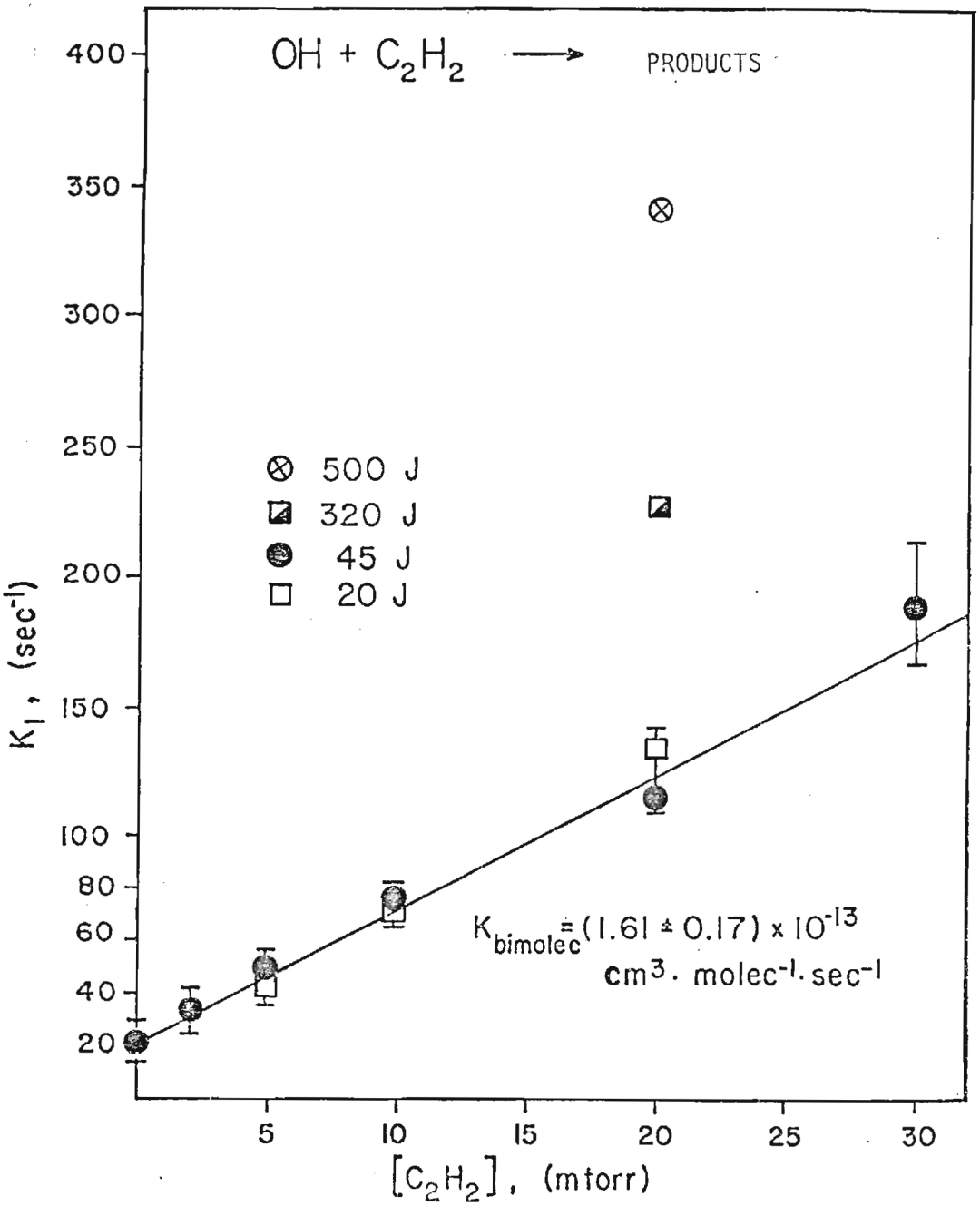


Figure 2. Kinetics of the OH + C_2H_2 reaction. A plot of the pseudo-first order rate constant as a function of both acetylene pressure and flash energy.

and the concentrations of these species in the reaction cell).

$$C_2H_2 + h\nu \longrightarrow C_2H + H \qquad (11)$$

Therefore, even if C_2H reacted on every collision with OH radicals, this should not cause a significant increase in the net rate of removal of OH. The H atoms formed in the photolysis of H_2O are initially produced with a concentration equal to that of the hydroxyl radicals, and can react with acetylene to form C_2H_3:

$$H + C_2H_2 \xrightarrow{M} C_2H_3 \ . \qquad (12)$$

The rate constant data for reaction (12) published by different workers are not in good agreement[27-30]; and consequently, the equivalent bimolecular rate constant at 100 Torr total pressure is not well established. It could be as high as 10^{-12} cm^3 $molecule^{-1}$ sec^{-1}. The product, C_2H_3, is expected to be highly reactive towards OH radicals.

A further process which could be important in the removal of OH radicals is that involving OH radicals reacting with the primary product of reaction (2). For example,

$$OH + C_2H_2O \longrightarrow C_2HO + H_2O \ . \qquad (13)$$

Again the rate constant for this process could be expected to be rapid. The overall rate of removal of OH can now be expressed as:

$$-d[OH]/dt = k_2[OH][C_2H_2] + k'[OH][C_2H] + k''[OH][C_2H_3] + k'''[OH][C_2H_2O] \ .$$

It can be seen that all processes, except for (2), depend upon the square power of the flash intensity. It has been shown by these authors, using the above kinetic scheme, that when $[OH]_0 = (1.5\text{-}3.5) \times 10^{11}$ radical cm^{-3} there appears to be no significant perturbation due to secondary processes; whereas, when $[OH]_0 = (2.3\text{-}3.6) \times 10^{12}$ radical cm^{-3}, the experimental data and computer

model calculations show the presence of significant secondary processes.

Other reactions of possible significance could involve electronically excited $C_2H_2^*$,

$$C_2H_2^* + OH \longrightarrow \text{Products} \quad (14)$$

$$C_2H_2^* + C_2H_2 \longrightarrow C_4H_4^* \text{ , etc.} \quad (15)$$

These species are thought to be long-lived enough to participate in reactions with OH.[31] Also, since excited $C_2H_2^*$ is formed at long wavelengths where the light flux from the flash lamp is more intense, these reactions could have been of significant importance to the observed flash dependence of the first-order rate constants.

At flash energies $\leq$ 45 J and for total pressures ranging from 20 to 500 Torr of He, the bimolecular rate constant k_2 was found to be $1.65 \pm 0.15 \times 10^{-13}$ cm^3 $molecule^{-1}$ sec^{-1} independent of the total pressure.

DISCUSSION OF PREVIOUS WORK

A. $OH_2 + C_2H_4 \longrightarrow$ products

There have been six room-temperature studies of Reaction (1).[3-5,14-16] The earliest study was performed by Wilson and Westenberg[16] using a discharge-flow system coupled with ESR detection of OH. They reported a value for k_1 of $5 \times 10^{-12}/n$ cm^3 molecule^{-1} .sec^{-1}; where n is a stoichiometric correction factor which represents the number of OH radicals that react for each initial C_2H_4 that reacts (i.e., n >1 due to OH reacting with species produced in the primary and subsequent processes). Considering the low pressures utilized in flow systems, the value of n which is required in order to bring their results into agreement with the present study would have to be approximately 2.

Greiner,[4] utilizing kinetic absorption spectroscopy, reported a value for k_1 of 5×10^{-12} cm^3 molecule^{-1}.sec^{-1}. No mention was made of the total pressure used in his system. The experimental data was corrected in order to allow for secondary reactions caused by reaction products. However, it was assumed that the photolysis products of ethylene would not cause any appreciable increase in the rate of removal of OH radicals. This assumption appears to be valid in that the photolysis products of C_2H_4 are probably C_2H_2 and H_2, and these both react slower with OH radicals than does C_2H_4. Also, if the total pressure in his system was 100 torr, as was used in previous studies,[1,2,32] then the results obtained are in substantial agree-

ment with those obtained in the present study at 100 torr total pressure of He.

Morris, Stedman, and Niki[3] used a discharge-flow system at 1 torr total pressure of He coupled with mass spectrometric detection of OH under both ethylene-rich and OH-rich conditions. Their value of $k_1=1.8\times10^{-12}cm^3$ $molecule^{-1}.sec^{-1}$, obtained by monitoring C_2H_4 in the presence of an excess concentration of OH radicals, is in substantial agreement with our experimental value of k_1 at 3 torr total He pressure. This study did not require a stoichiometric correction factor, as the primary products of Reaction (1) would preferentially react with the excess concentration of OH radicals and not with the C_2H_4 which was being monitored. The value reported for the ethylene-rich system, where OH radicals were monitored, was $2.5/n\times10^{-12}cm^3$ $molecule^{-1}.sec^{-1}$. No value was reported for n.

Stuhl,[14] utilized the resonance fluorescence technique to monitor hydroxyl radicals in the presence of an excess concentration (>100) of C_2H_4 and obtained a value for k_1 of $3\pm1\times10^{-12}cm^3$ $molecule^{-1}.sec^{-1}$at 300°K and 20 torr total pressure of He. This value is slightly lower than that obtained in the present study at the same total pressure, $k_1=4.1\pm0.2\times10^{-12}cm^3$ $molecule^{-1}.sec^{-1}$. However, it can be seen that the two values are in agreement within the expressed uncertainties. Secondary reactions were shown to be unimportant under their experimental conditions. No mention of any pressure dependence was noted by Stuhl.

Smith and Zellner[15] used the flash photolysis-resonance absorption technique to study Reaction (1) in a static cell at either, (a) 10-20 torr total pressure of He or, (b) 10 torr of H_2 and 10 torr of N_2O. High initial concentrations of hydroxyl radicals were used ($[OH]_o\leq3\times10^{13}$radical cm^{-3}), but

the authors reported that this did not lead to the presence of complicating secondary reactions. They found a value for k_1 of 5.2×10^{-12} cm^3 $molecule^{-1}.sec^{-1}$ which was invariant with total pressure or diluent gas. Although the value obtained in the present study with 20 torr of He ($k_1 = 4.2 \pm 0.2 \times 10^{-12}$ cm^3 $molecule^{-1}.sec^{-1}$) is within 25% of their value, it is felt that the two studies are not in particularly good agreement as N_2O would be expected to be a more efficient third body than He.

Bradley et al.[5] studied Reaction (1) in a discharge flow system at 3 torr total pressure (He), using ESR detection of hydroxyl radicals. Low initial stoichiometries, ($[C_2H_4]_o/[OH]_o = 5.5 = 13.1$) were used, which resulted in a stoichiometric correction factor, n, being required to allow for secondary removal of hydroxyl radicals. A mass spectrometric end product analysis yielded a value of 2.6 for n, which when combined with the experimental value of k_1/n, produced a value of $1.67 \pm 0.5 \times 10^{-12}$ cm^3 $molecule^{-1}.sec^{-1}$ for k_1. This value is slightly lower than that obtained in the present study at 3 torr of He, but within the reported experimental uncertainties of the two studies.

In summary, from an examination of all the previous data on k_1 it is seen that when the pressure dependence of Reaction (1) is considered, the previously published results are in reasonably close agreement.

B. $OH + C_2H_2 \longrightarrow$ products

Of the room temperature studies of Reaction (2) that have been reported, the ealiest work was done by Wilson and Westenberg[16] utilizing ESR detection of OH generated by the reaction $H + NO_2 \rightarrow OH + NO$ in a fast flow system. They obtained the result that $k_2 = 1.0 \times 10^{-12}/n$ cm^3 $molecule^{-1}.sec^{-1}$, where n is

a stoichiometric correction factor. For there to be substantial agreement between the present work and that of Wilson and Westenberg, a stoichiometric correction factor of 5-6 would have to be employed. This correction appears to be too large and does not fully account for the difference between the two measurements.

A measurement by Breen and Glass [17] is in better agreement with the present work. They used a discharge-flow system coupled with ESR detection of OH which was again produced from the H/NO_2 reaction. A stoichiometry correction factor of 2 was required for OH consumption via secondary reactions. This was obtained from a mass spectrometric analysis of the end products of the reaction. The rate of consumption of OH radicals in the presence of an excess concentration of C_2H_2($[C_2H_2]_o/[OH]_o$ 3.7-57.0) was monitored via ESR detection, and the decay curve was modeled with an assumed kinetic scheme to calculate $k_2(eff)=k_2/n$ (n = stoichiometric correction factor). From the values of $k_2(eff)$ and n, a value of $1.9\pm0.6\times10^{-13}$ cm^3 $molecule^{-1}.sec^{-1}$ was obtained. This value is in good agreement with that obtained from the present study.

A study of Reaction (2) was performed by Smith and Zellner utilizing the flash photolysis-resonance absorption technique. They obtained a bimolecular rate constant of 8.7×10^{-13} cm^3 $molecule^{-1}.sec^{-1}$, a result which is approximately a factor of 5 higher than that obtained in the present work. High flash energies on the order of 180-500 J were used, producing initial hydroxyl radical and hydrogen atom concentrations of $\leq3\times10^{13}$ radical cm^{-3}. This could have resulted in secondary processes becoming a highly significant perturbation in their system even though their initial $[C_2H_2]_o/[OH]_o$ ratio was typically 100 (estimated from the experimental data given in their paper).

Thus, the stoichiometric correction factor could have been quite large. This line of argument presupposes that the secondary reactions of C_2H_3 (from reaction of H and C_2H_2) and C_2H_2O with OH radicals are rapid.

Recently Pastrana and Carr[18] studied Reaction (2) in a flow system utilizing resonance line absorption detection of OH. Acetylene to OH ratios of (a) 2.3-13.2 and (b) 14-125 were used in two separate studies. The values obtained for the bimolecular rate constant k_2 were $(2.9\pm0.3)/nx10^{-13}$ and $(2.1\pm0.6)/nx10^{-13}$ cm^3 $molecule^{-1}.sec^{-1}$, respectively, where n is the stoichiometric correction factor. They assumed that n had a value of 2.1 (as measured by Breen and Glass[17]) in series (a), yielding a bimolecular rate constant of $(1.4\pm0.3)x10^{-13}$ cm^3 $molecule^{-1}.sec^{-1}$. In series (b) they assumed that experimental conditions were such that secondary processes would be of less significance and that n would have a value close to unity. Although secondary reactions may not be so important in series (b), it is quite conceivable that n could be significantly greater than unity. The overall value reported for k_2 was $(2.0\pm0.6)x10^{-13}cm^3$ $molecule^{-1}.sec^{-1}$. It can be seen that this value is in good agreement with that obtained in the present study.

In summary, the present study has shown that there is no pressure dependency for the rate of Reaction (2). However, the rate of removal of hydroxyl radicals is extremely sensitive to secondary reactions. The species most likely to participate in secondary removal of OH are: (a) the primary product of Reaction (2), e.g., C_2H_2O and (b) the C_2H_3 radical formed in the H + acetylene reaction. The value reported for k_2 in the present study was obtained using low flash energies and therefore should be free of any significant perturbation due to secondary processes.

SECTION 4

A KINETICS STUDY OF THE REACTION OF OH RADICALS WITH AROMATICS AND OLEFINS

INTRODUCTION

The hydroxyl radical is known to be one of the most reactive species in the atmosphere.[33] In particular, its reaction with hydrocarbons in the troposphere is believed to be the key initiating step in the oxidation of these compounds, thereby leading to the formation of ozone via a complex chemical degradation cycle involving NO_x species.[33] Thus, since recent measurements have indicated the presence of a considerable amount of aromatic and olefinic hydrocarbons in the troposphere,[34] it is apparent that an understanding of the reactivity of OH with hydrocarbons is essential to a realistic evaluation of the ozone budget in both the perturbed and the unperturbed troposphere. In addition to its key importance in the field of tropospheric chemistry, OH-hydrocarbon reactions are also of crucial importance in combustion systems.[35]

There have been numerous rate constant measurements for the reaction of hydroxyl radicals with a variety of hydrocarbons.[36] Whereas reasonably good agreement exists for the reaction rate constants for OH plus saturated hydrocarbons, very little agreement can be found for those rate constants measured for OH-olefin processes. In the case of aromatic species, there is a major absence of data, especially involving substituted aromatic hydrocarbons. For this reason, we have initiated a new study to determine the

rate constants for the reactions of the hydroxyl radical with both olefinic and aromatic hydrocarbons. The data for olefin reactions were presented in an ACS meeting.[50] Those reactions investigated include:

OH + o-xylene	⟶	products	(1)
OH + m-xylene	⟶	products	(2)
OH + p-xylene	⟶	products	(3)
ethylbenzene	⟶	products	(4)
n-propylbenzene	⟶	products	(5)
isopropylbenzene	⟶	products	(6)
hexafluorobenzene	⟶	products	(7)
n-propyl hexafluorobenzene	⟶	products	(8)
propylene	⟶	products	(9)
1-butene	⟶	products	(10)
cis-2-butene	⟶	products	(11)
tetramethylethylene	⟶	products	(12)

EXPERIMENTAL SECTION

The experimental details and operating principles of the flash photolysis-resonance fluorescence techniques have been fully described in the literature;[10,11,21] hence, only a brief summary will be presented in this text.

The reaction vessel used in this work was made of quartz and was equipped with either a calcium fluoride or a quartz window through which the photolyzing beam could enter the cell. As in earlier studies involving OH radicals, H_2O was photolyzed using a N_2 spark discharge lamp to produce a typical ground state OH concentration of 3×10^{11} cm^{-3}:

$$H_2O + h\nu \longrightarrow H + OH(X^2\Pi) \quad .$$

Excitation of OH was accomplished via the use of an OH resonance lamp. This lamp primarily produced the emission characteristic of the $(A\Sigma^{2+}:v'=0) \rightarrow (X^2\Pi:v''=0)$ transition of OH. A small fraction of the OH, produced by the photolysis of H_2O, was continuously excited by the emission from this lamp. Fluorescence from excited OH was measured using a photomultiplier tube located at right angles to the lamp. The intensity of this fluorescent emission was found to be directly proportional to the amount of OH present in the mixture. The fluorescence signal from the photomultiplier tube was then stored as a function of time in a multichannel analyzer, operated in the multiscaling mode.

Since the hydrocarbon pressures were in large excess relative to the OH concentration, the observed kinetic decays for reactions (1)-(12) were

pseudo-first order with respect to OH. Under typical operating conditions, the hydroxyl radical concentration was kept sufficiently low that the initial stoichiometry of the system (i.e., $[\text{hydrocarbons}]_0/[OH]_0$) was always greater than 50. Because of the low initial OH concentration, multiple flashes (<60) on each of many identical gas mixtures were required to produce a single smooth kinetic decay curve. The pseudo-first order rate constants were then obtained from a least square analysis of a plot of the logarithm of the count rate in each channel of the analyzer (after the background was subtracted) vs. time. The bimolecular rate constants were obtained from a least squares treatment of the slope of the line obtained from a plot of the pseudo-first order rate constants vs. hydrocarbon concentrations.

Gas pressures of less than 3 Torr were measured using an MKS Baratron pressure gauge which was periodically checked against a dibutyl phthalate manometer. The high pressure measurements (10-800 Torr) were made with a two-turn Bourdon gauge (Wallace and Tierman type FA-145). The precision to which gas mixtures could be made, with the exception of H_2O, was determined to be ~3% or better. The H_2O pressure could not be metered so precisely because of absorption effects on the surfaces of the reaction cell. In the latter case, the precision was between 10-20%.

The purity of each of the hydrocarbons used in this study was as follows: propene (Matheson, 99.7%), 1-butene (Matheson, 99.9%), cis-2-butene (Matheson, 99.9%), tetramethylethylene (Aldrich Chem. Co., >99%), ethyl benzene (Baker-Ultrex, 99.99%), n-propyl benzene (Baker-Ultrex, 99.9%), isopropyl benzene (Baker-Ultrex, 99.97%, o-xylene (Baker-Ultrex, 99.99%), m-xylene (Baker, >96%), p-xylene (Baker-Ultrex, 99.99%), hexafluorobenzene (PCR, >99.7%), n-propyl hexafluorobenzene (PCR, >94%, the main impurity is isopropyl hexafluorobenzene).

All hydrocarbons were subjected to multiple freeze-pump-thaw cycles before use. The olefins were checked for their purity using a mass spectrometer. Matheson gold label high-purity helium and argon were used without further purification. The H_2O used in this study was double distilled and before use was subjected to two freeze-pump-thaw cycles.

RESULTS AND DISCUSSION

The results from this investigation have been summarized in Tables I-XII. For most of the reactions studied, a wide range of experimental conditions was covered in order to verify that kinetic complications due to secondary processes were not affecting the observed OH decay rates. These variations included changing the photo-flash energy, the total pressure of the system, the hydrocarbon reactant gas pressure, and the number of flashes to which a given gas mixture was subjected. Since the initial concentrations of both OH and photofragments from the hydrocarbon reactant would necessarily increase linearly with an increasing photolyzing photon flux(i.e.,the flash energy), the decay of OH via reaction with photofragments would depend on the square of the flash energy. If this path had been a significant fraction of the measured pseudo-first order rate constant, k', changes in the flash energy of a factor of four or more would have had a significant effect on the value of k'. As can be seen in Tables IV, V, VIII, X, and XI, this obviously was not the case in our study. (Even though flash variations were not performed on every compound investigated, the similarity of these compounds to those exposed to flash variations would strongly point to the absence of anomalous behavior for these other compounds.) Moreover, a calculation of the contribution of this type of radical-radical secondary reaction, even with the assumption that it occurs at gas kinetic collision rates, indicates that the process is unimportant under our experimental conditions. (In this calculation the absorption cross section for the hydrocarbons is assumed to be

TABLE I. Rate Data for the Reaction of OH with Ethylbenzene at 298°K

[Reactant] m Torr	[Diluent] Torr	Flash Energy,J	Flashes/ Filling	k',s^{-1}	k_{bi}, $cm^3 molecule^{-1} s^{-1}$
0	3 (He)	88	60	186	
0.23	3	88	60	250	
0.46	3	88	60	301	
1.00	3	88	60	430	$(7.50 \pm 0.38) \times 10^{-12}$
0	20 (He)	88	60	55	
0.25	20	88	60	125	
0.25	20	88	60	128	
0.50	20	88	60	183	
0.75	20	88	60	252	
0.75	20	88	60	240	
1.00	20	88	60	280	
1.50	20	88	60	406	$(7.06 \pm 0.26) \times 10^{-12}$
0.50	200 (He)	88	30	163	
0.50	200	88	30	160	
1.00	200	88	30	275	
1.50	200	88	30	419	
2.00	200	88	30	543	$(7.95 \pm 0.28) \times 10^{-12}$

The pressure of H_2O, the photolyte, was 200 m Torr.

TABLE II. Rate Data for the Reaction of OH with n-propylbenzene at 298°K

[Reactant] m Torr	[Diluent] Torr	Flash Energy,J	Flashes/ Filling	k',s^{-1}	k_{bi}, $cm^3 molecule^{-1} s^{-1}$
0	20 (He)	88	30	105	
0.25	20	88	60	157	
0.50	20	88	60	209	
0.75	20	88	60	256	
1.00	20	88	60	292	
1.25	20	88	60	375	$(6.40 \pm 0.36) \times 10^{-12}$
0	200 (He)	88	30	30	
0.25	200	88	60	85	
0.25	200	88	60	102	
0.50	200	88	60	135	
0.50	200	88	60	132	
0.75	200	88	60	175	
0.75	200	88	60	195	
1.00	200	88	60	243	
1.25	200	88	60	270	
1.25	200	88	60	275	
1.50	200	88	60	320	$(5.86 \pm 0.16) \times 10^{-12}$

The pressure of H_2O, the photolyte, was 200 m Torr.

TABLE III. Rate Data for the Reaction of OH with isopropylbenzene at 298°K

[Reactant] m Torr	[Diluent] Torr	Flash Energy,J	Flashes/ Filling	k',s^{-1}	k_{bi}, $cm^3 molecule^{-1} s^{-1}$
0	200 (He)	88	30	34	
0.25	200	88	60	99	
0.50	200	88	30	164	
0.50	200	88	100	170	
0.75	200	88	60	206	
1.00	200	88	60	275	
1.00	200	88	60	305	
1.25	200	88	60	374	
1.50	200	88	60	396	$(7.79 \pm 0.40) \times 10^{-12}$

The pressure of H_2O, the photolyte, was 200 m Torr.

TABLE IV. Rate Data for the Reaction of OH with n-propyl pentafluorobenzene at 298°K

[Reactant] m Torr	[Diluent] Torr	Flash Energy,J	Flashes/ Filling	k',s^{-1}	k_{bi}, $cm^3 molecule^{-1} s^{-1}$
0	3 (He)	88	60	208	
0.5	3	88	60	255	
1.0	3	88	60	316	
1.5	3	88	60	323	$(2.52 \pm 0.54) \times 10^{-12}$
0	20 (He)	88	60	80	
0.5	20	88	60	139	
1.0	20	88	60	180	
1.0	20	40	60	185	
1.0	20	245	60	181	
1.5	20	88	60	246	
2.0	20	88	60	315	
2.5	20	88	60	330	
3.0	20	88	60	357	$(3.01 \pm 0.76) \times 10^{-12}$
0	200 (He)	88	60	45	
0.5	200	88	60	85	
1.0	200	88	60	160	
1.5	200	88	60	184	
1.5	200	40	60	170	
1.5	200	245	60	195	
2.0	200	88	60	248	
2.5	200	88	60	290	$(3.06 \pm 0.24) \times 10^{-12}$

The pressure of H_2O, the photolyte, was 200 m Torr.

TABLE V. Rate Data for the Reaction of OH with Hexafluorobenzene at 298°K

[Reactant] m Torr	[Diluent] Torr	Flash Energy,J	Flashes/ Filling	k',s^{-1}	k_{bi}, $cm^3 molecule^{-1} s^{-1}$
0	20 (He)	88	60	70	
5	20	88	60	109	
10	20	88	60	164	
15	20	88	60	179	
15	20	40	60	184	
20	20	88	60	211	
25	20	88	60	248	
30	20	88	60	319	
40	20	88	60	346	$(2.21 \pm 0.20) \times 10^{-13}$
15	20 (He)	245	60	230	
0	200 (He)	88	60	34	
5	200	88	60	75	
10	200	88	60	117	
10	200	40	60	108	
15	200	88	60	152	
20	200	88	60	196	
30	200	88	60	240	$(2.19 \pm 0.16) \times 10^{-13}$
10	200 (He)	245	60	135	

The pressure of H_2O, the photolyte, was 200 m Torr.

TABLE VI. Rate Data for the Reaction of OH with o-Xylene at 298°K

[Reactant] m Torr	[Diluent] Torr	Flash Energy, J	Flashes/ Filling	k', s^{-1}	k_{bi}, $cm^3 molecule^{-1} s^{-1}$
0	20 (He)	88	30	48	
0.5	20	88	30	266	
1.0	20	88	30	476	
1.5	20	88	30	680	$(1.29 \pm 0.01) \times 10^{-11}$
0	20 (Ar)	88	30	33	
0.5	20	88	30	250	
0.5	20	88	100	250	
0.5	20	88	200	256	
0.5	20	30	30	242	
1.0	20	88	30	451	$(1.30 \pm 0.03) \times 10^{-11}$
0	200 (He)	88	30	48	
0.5	200	88	30	255	
1.0	200	88	30	455	$(1.24 \pm 0.01) \times 10^{-11}$

The pressure of H_2O, the photolyte, was 200 m Torr.

TABLE VII. Rate Data for the Reaction of OH with m-Xylene at 298°K

[Reactant] m Torr	[Diluent] Torr	Flash Energy,J	Flashes/ Filling	k',s^{-1}	k_{bi}, $cm^3 molecule^{-1} s^{-1}$
0	3 (Ar)	88	30	81	
0.333	3	88	30	256	
0.667	3	88	30	400	
1.0	3	88	30	629	
1.5	3	88	30	830	$(1.56 \pm 0.14) \times 10^{-11}$
0	20 (Ar)	88	30	41	
0.5	20	88	30	365	
0.75	20	88	30	539	
1.0	20	88	30	658	
1.5	20	88	30	999	$(1.94 \pm 0.08) \times 10^{-11}$
0	20 (He)	88	30	41	
0.5	20	88	30	406	
1.0	20	88	30	761	
1.5	20	88	30	1095	$(2.14 \pm 0.02) \times 10^{-11}$
0	200 (Ar)	88	30	20	
0.25	200	88	30	194	
0.50	200	88	30	350	
0.75	200	88	30	479	
1.0	200	88	30	742	
1.5	200	88	30	1000	$(2.03 \pm 0.19) \times 10^{-11}$
0	200 (He)	88	30	50	
0.50	200	88	30	424	
0.75	200	88	30	534	
1.0	200	88	30	787	
1.5	200	88	30	1048	$(2.06 \pm 0.13) \times 10^{-11}$

The pressure of H_2O, the photolyte, was 200 m Torr.

TABLE VIII. Rate Data for the Reaction of OH with p-Xylene at 298°K

[Reactant] m Torr	[Diluent] Torr	Flash Energy,J	Flashes/ Filling	k',s^{-1}	k_{bi}, $cm^3 molecule^{-1} s^{-1}$
0.188	3 (Ar)	88	60	312	
0.25	3	88	60	345	
0.50	3	88	60	395	
0.75	3	88	60	482	$(8.8 \pm 1.2) \times 10^{-12}$
0	20 (He)	88	60	89	
0.25	20	88	60	162	
0.50	20	88	60	259	
0.50	20	88	25	287	
0.50	20	30	60	253	
0.75	20	88	60	315	
1.00	20	88	60	464	
1.25	20	88	60	520	$(1.01 \pm 0.10) \times 10^{-11}$
0	200 (He)	88	60	92	
0.25	200	88	60	193	
0.50	200	88	60	289	
0.75	200	88	60	392	
1.00	200	88	60	452	
1.25	200	88	60	545	
1.50	200	88	60	591	$(1.05 \pm 0.06) \times 10^{-11}$

The pressure of H_2O, the photolyte, was 200 m Torr.

TABLE IX. Rate Data for the Reaction of OH with Propylene at 298°K

[Reactant] m Torr	[Diluent] Torr	Flash Energy,J	Flashes/ Filling	k',s^{-1}	k_{bi}, $cm^3 molecule^{-1} s^{-1}$
0	20 (He)	88	50	55	
0.25	20	88	50	274	
0.50	20	88	50	446	
0.75	20	88	50	622	
1.00	20	88	50	926	
1.25	20	88	50	1060	
1.50	20	88	50	1316	$(2.56 \pm .12) \times 10^{-11}$
0	200	88	50	33	
0.5	200	88	50	412	
0.75	200	88	50	619	
1.00	200	88	50	910	$(2.63 \pm .12) \times 10^{-11}$

The pressure of H_2O, the photolyte, was 200 m Torr.

TABLE X. Rate Data for the Reaction of OH with 1-Butene at 298°K

[Reactant] m Torr	[Diluent] Torr	Flash Energy, J	k', s^{-1}	k_{bi}, $cm^3 molecule^{-1} s^{-1}$
0	3	88	210	
.2	3	88	380	
.4	3	88	590	
.6	3	88	790	$(2.96 \pm .19) \times 10^{-11}$
0	20	88	77	
.2	20	88	280	
.4	20	88	447	
.4	20	45	465	
.4	20	180	480	
.4	20	281	410	
.4	20	88	430*	
.4	20	88	405**	
.6	20	45	640	
.8	20	88	840	$(2.94 \pm .14) \times 10^{-11}$

* 20 flashes/filling
**200 flashes/filling
The pressure of H_2O, the photolyte, was 200 m Torr , the number of flashes/filling was 50.

TABLE XI. Rate Data for the Reaction of OH with *cis*-2-Butene at 298°K

[Reactant] m Torr	[Diluent] Torr	Flash Energy, J	k', s^{-1}	k_{bi}, $cm^3 molecule^{-1} s^{-1}$
0	3	88	210	
.2	3	88	490	$(4.32 \pm .41) \times 10^{-11}$
0	20	88	68	
.1	20	88	190	
.2	20	88	350	
.2	20	45	360	
.2	20	180	380	
.4	20	88	620	
.4	20	180	620	
.6	20	88	890	$(4.26 \pm .25) \times 10^{-11}$

The pressure of H_2O, the photolyte, was 200 m Torr, the number of flashes/filling was 20.

TABLE XII. Rate Data for the Reaction of OH with Tetramethylethylene at 298°K

[Reactant] m Torr	[Diluent] Torr	Flash Energy,J	k',s^{-1}	k_{bi}, $cm^3 molecule^{-1} s^{-1}$
0	20	88	68	
.1	20	88	250	
.2	20	88	430	
.3	20	88	620	$(5.69 \pm .13) \times 10^{-11}$

The pressure of H_2O, the photolyte, was 200 m Torr, the number of flashes/filling was 20.

$< 4 \times 10^{-16}$ cm^2). A similar type calculation shows that the products of the OH-hydrocarbon reactions are also not of any significance.

Variation of the number of flashes on a given gas mixture was carried out to determine if: (a) final stable reaction products could be influencing the measured k' values; and (b) reactants were being depleted during multiple flashing. The results (see Tables I, II, III, VI, and VIII) show that neither of the above possibilities were significant. In the case of tetramethylethylene, however, no such variations were carried out. However, the number of flashes per filling were minimal.

Finally, concerning other possible radical-radical reactions involving OH, H, and O, viz:

$$OH + OH \longrightarrow H_2O + O$$

$$O + OH \longrightarrow O_2 + H \quad ,$$

we have previously shown that these processes are unimportant under the conditions employed in this study.

Substituted Aromatics

In Table XIII we have listed the rate constants measured in this work for three xylenes, three monosubstituted benzenes, and two monosubstituted pentafluoro benzenes at different pressures. Also included in Table XIII are the results of several other investigators which have appeared in the literature. As can be seen in this table, we have covered a wide range of diluent gas pressures (3 Torr to 200 Torr) and have also used two different diluent gases, argon and helium.

The rate constant for the OH-o-xylene system, k_1, was found to be pressure independent between 20 and 200 Torr, indicating that k_1 was near or at its

TABLE XIII. Summary of Rate Data for OH + Aromatics

AROMATIC HYDROCARBON	$k \times 10^{12}$ cm^3 molecule^{-1} s^{-1}						
	THIS WORK	SECTION 2	REF. (38)	REF. (51)	REF. (37)	REF. (39)	REF. (40)
o-Xylene	12.9 ± .1 (20 Torr He) 13.0 ± .3 (20 Torr Ar) 12.4 ± .1 (200 Torr He)		15.3 ± 1.5	12.8 ± 3.8	14.3 ± 1.5		
m-Xylene	15.6 ± 1.4 (3 Torr Ar) 19.4 ± .8 (20 Torr Ar) 21.4 ± .2 (20 Torr He) 20.3 ± 1.9 (200 Torr Ar) 20.6 ± 1.3 (200 Torr He)		23.6 ± 2.4	23.2 ± 1.7	24.0 ± 2.5		18.7 (a mixture of all 3 isomers)
p-Xylene	8.8 ± 1.2 (3 Torr Ar) 10.1 ± 1.0 (20 Torr He) 10.5 ± .6 (200 Torr He)		12.2 ± 1.2	12.3 ± 2.5	15.3 ± 1.7		
Ethylbenzene	7.5 ± .38 (3 Torr He) 7.06 ± .26 (20 Torr He) 7.95 ± .28 (200 Torr He)					8.7	
Hexafluorobenzene	.221 ± .020 (20 Torr He) .219 ± .016 (200 Torr He)						
n-propylbenzene	6.40 ± .36 (20 Torr He) 5.86 ± .16 (200 Torr He)					6.8	
isopropylbenzene	7.79 ± .40 (200 Torr He)					6.7	
n-propylpentafluoro-benzene	2.52 ± .54 (3 Torr He) 3.01 ± .76 (20 Torr He) 3.06 ± .24 (200 Torr He)						
Benzene		.849 ± .08 (3 Torr He) 1.36 ± .09 (20 Torr He) 1.59 ± .12 (100 Torr He)					
Toluene		3.60 ± .26 (3 Torr He) 5.00 ± .18 (20 Torr He) 6.11 ± .40 (100 Torr He)					

high pressure limit. For the compounds m-xylene and p-xylene, lower total pressures were employed (i.e., 3 Torr); in this case, the measured rate constants at 3 Torr of argon were slightly less than those measured at 20 and 200 Torr. This observed change in k with pressure would definitely appear to be outside the experimental error limits of the measurements. Thus, the indications are that the high pressure limit for the OH-xylene addition reaction is in the vicinity of 3 Torr. In the case of ethylbenzene, on the other hand, the 3 Torr rate constant is,within experimental error,the same as that at 20 and 200 Torr of helium. The same trend holds for the other four compounds studied, namely, hexafluorobenzene, n-propyl benzene, isopropylbenzene and n-propyl pentafluorobenzene.

On the basis of the rate data presented, one would conclude that the reactions of OH withsubstituted aromatics studied in this investigation reach the high pressure limit at or near 3 Torr. This observation of a reduced high pressure limit for both the disubstituted and the higher molecular weight monosubstituted aromatics relative to benzene and toluene is consistent with that expected from the unimolecular theory of reaction rates which predicts a lower value for the high pressure limit of a third order reaction when the number of vibrational degrees of freedom of the transition state complex increases.

The rate data obtained by Perry, et al.,[37] Hansen, et al.,[38] and Lloyd, et al.,[39] for o-xylene,m-xylene, and p-xylene agree, within experimental error,with those obtained in this work. These first two studies were performed using flash photolysis-resonance fluorescence technique, while the third investigation utilized an environmental chamber. The rate constant obtained by Morris and Niki[40] for a mixture of the three xylenes is, within experimental error, also the same as that obtained in this study. In the

experiment by Morris and Niki a discharge flow-mass spectrometer system was used. For the compounds ethylbenzene, n-propylbenzene and isopropylbenzene, there is only one set of data reported in the literature. These results were obtained by Lloyd, et al.[39] by measuring the rate of disappearance of these aromatics relative to that of n-butane in an environmental chamber.

In our study, we have investigated a series of substituted aromatic hydrocarbons including those where the hydrogen atoms on the aromatic ring have been altered. As can be seen from Table XIII, the replacement of all the hydrogen atoms in the benzene ring with fluorine atoms reduces the reaction rate of this aromatic with OH by a factor of 6. (The rate constant for the OH-benzene reaction is 1.59×10^{-12} cm^3 $molecule^{-1}$ s^{-1} as compared to 0.2×10^{-12} cm^3 $molecule^{-1}$ s^{-1} for OH-hexafluorobenzene.) We attribute this reduction in reactivity solely to the depletion of the electron density on the aromatic ring which would affect the extent of electrophilic addition of the OH radical.

As shown in our earlier study (see Section 2), a comparison of the reactivity of hydroxyl radicals with benzene and toluene reveals that the addition of a methyl group to the aromatic ring increases the rate constant of the OH-aromatic reaction by a factor of $\sim$4. Moreover, the rate constant for the reaction of OH with toluene increases by a factor of 2 between 3 and 100 Torr. Based on these observations, these authors concluded that the addition of OH to the ring was the predominant reaction and the abstraction was less than 50%. A further increase in the chain length of the substituent on the aromatic ring does not change its reaction rate with hydroxyl radicals to a significant extent. This point is illustrated here in Table XIII, where it is seen that the rate constant for the reactions of OH with ethylbenzene, n-propylbenzene, and

isopropylbenzene are essentially the same. This invariance of the rate constant as a function of the chain length of the substituent indicates that the abstraction of a hydrogen atom from the side chain is not a significant fraction of the total reaction of these aromatics with OH. This conclusion is in agreement with the known electron donating characteristics of these substituents to aromatic rings, as reflected in their similar Hamett constant values.[41] To further test this hypothesis, we have measured the rate constant for the reaction of hydroxyl radical with n-propyl pentafluorobenzene. If the abstraction of a hydrogen atom from the side chain was a very significant part of the reaction, the fluorination of the aromatic ring would not decrease the rate constant for the reaction significantly. However, we found that n-propyl pentafluorobenzene reacted with OH about half as fast as did n-propyl benzene. This decrease in rate constant would put a maximum limit of 50% on the abstraction route. (Hexafluorobenzene itself reacts with OH about 1/6 as fast as does benzene.) It should be noted that n-propyl pentafluorobenzene reacts as fast as 3×10^{-12}; this could be partially explained by assuming that the propyl side chain donates a significant amount of electron density back to the aromatic ring.

The above proposition that addition is the main route for the reaction of OH radicals with substituted benzenes is further substantiated when one examines the relative reactivity of the three xylenes with OH. It is well known that the electron donating ability of a substituent to an aromatic ring is very sensitive to the position of the substitution. In the case of o-, p-, and m-xylene the number of abstractable hydrogen atoms is the same and, in all three cases, the C-H bond energies on the methyl group are equal. Yet m-xylene was found to react almost 1.5 times faster than both o- and p-

xylene. Hence, as noted in our ealier work, we must conclude that the addition of OH to the ring takes place because of the electrophilic nature of the OH.

Our conclusions, presented above, are in good agreement with those of Perry, et al.[37] They measured the temperature dependencies for these reactions of OH with benzene, toluene, and o-, m-, and p-xylene. These authors concluded that at lower temperatures, namely betwen 296K and 325K, the OH reaction ocurred both via the addition and abstraction mode. These conclusions were based on the signs of the activation energies in the two temperature regimes (viz, 296-325K and 380-473K) and an interpretation of the non-exponential behavior of OH consumption in the intermediate temperature range of 325 to 380K. Based on their rate data, Perry, et al. have estimated the branching ratios for the two reaction pathways (k addition/k abstraction) at 298K to be 5, 4, 24, and 14 for toluene, o-xylene, m-xylene, and p-xylene, respectively. These numbers are within the range estimated in our earlier study (Sec. 2).

The above authors attempted to further check their inference by studying the OH-perdeuterotoluene reaction, where they observed significant kinetic isotope effect only at 432K. Perry, et al., however, have not tried to correlate the values of the rate constants for different aromatic hydrocarbons at room temperatures with the substitution of the aromatic ring and the resulting change in the electron density on the aromatic ring.

OH + Propylene $\longrightarrow$ Products

Our measured value of the rate constant for the reaction of OH with propylene is independent of pressure between 20 and 200 Torr of He, with an average value of 2.6×10^{-11} cm^3 molecule^{-1} s^{-1} for k_9. Table XIV summarizes the results on the OH-propylene system obtained in the present work as well

TABLE XIV. Summary of Rate Data for OH + Olefin

AROMATIC HYDROCARBON	$k \times 10^{11}$ cm^3 $molecule^{-1}$ s^{-1}						
	THIS WORK	REF. (42)	REF. (14)	REF. (3)	REF. (40)	REF. (5)	REF. (43)
Propylene	2.56 ± .12* (20 Torr He) 2.63 ± .12 (200 Torr He)	2.51 ± .25 (25-100 Torr Ar)	1.45 ± .22	1.7 ± .4	1.7	.50 ± .17	0.5 ± 0.1
1-Butene	2.96 ± .19 (3 Torr He) 2.94 ± .14 (20 Torr He)	3.53 ± .36 (50 Torr Ar)			4.1		1.5 ± 0.1
Cis-2-Butene	4.32 ± .41 (3 Torr He) 4.26 ± .25 (20 Torr He)	5.37 ± .54 (50 Torr Ar)			6.1		
Tetramethylethylene	5.69 ± .13 (20 Torr He)				15.3		

*In References 42 and 50, it has been reported that we obtained a value of 1.59×10^{-11} for this rate constant. Subsequent to this measurement, we found that absorption of propylene on the walls of the metallic reaction cell was responsible for the lower value.

as those from six other studies.[3,5,14,40,42,43] Not reported in this table are the values of 1.1×10^{-11} and 1.34×10^{-11} cm^3 $molecule^{-1}$ s^{-1} obtained by Simonaitis and Heicklen,[44] and Gorse and Volman,[8] respectively. Both these investigations were competitive kinetics studies where k_9 was measured relative to the OH+CO reaction.It is apparent that both these values are approximately a factor of 2 lower than the results obtained in this study. It is possible that the reason for this discrepancy lies in a higher value for the rate constant of the OH + CO reaction at higher pressures.

Our value of 2.6×10^{-11} for k_9 agrees extremely well with that obtained by Atkinson and Pitts[42] who also utilized the technique of flash-photolysis resonance fluorescence. However, Stuhl[14] employed the same technique of flash-photolysis resonance fluorescence, and obtained a value of $1.45 \pm .22 \times 10^{-11}$ cm^3 $molecule^{-1}$ s^{-1}. We believe that this lower value could be due to the loss of propylene to metallic walls of the reaction vessel. Previous investigations in our laboratory utilizing an aluminum reactor have clearly shown absorption of reactants on walls to be a serious problem.

The last four columns in Table XIV are results obtained in low pressure flow systems. These low pressure results are lower than our value of k_9 by factors of 1.5-5. The reaction of OH with propylene has been assumed to occur through the abstraction of a hydrogen atom. We believe, however, that under high pressure conditions, these reactions proceed mainly by addition of OH to the double bond. Our results indicate that the addition reaction has reached its high pressure limit even below 20Torr.However,we cannot explain the large discrepancy between the low pressure flow tube data and the high pressure resonance fluorescence data solely on the basis of the addition reaction. It is our contention that part of this disparity is due to complicating chemistry

in the flow tube which would affect the estimated stoichiometric correction factors as well as to the fact that the addition reaction is still in the fallout region.

In the work by Slagle, et al.[45] where these authors carried out the direct identification of reaction channels in the reactions of hydroxyl radicals with propylene, the results suggest that even in the case of this olefin the abstraction of an allylic hydrogen by the OH radical is predominant. This, of course, would be incompatible with our conclusion. More recently these authors[46] have suggested , and we concur, that the explanation for this contradictory observation by Slagle, et al., can be found in a more detailed examination of their experimental conditions. In the latter work, the authors crossed a "molecular beam" of OH with a propylene beam and detected the products of the reaction utilizing photoionization mass spectrometry. The pressure in the reaction region was approximately 10^{-2} to 10^{-3} Torr. If we were to assume a reasonable value of 10^5 cm s^{-1} for the velocity of the molecular beam,it can be estimated that the time spent by the product in the "high pressure region" ($<10^{-2}$ Torr) is approximately a few microseconds. Under these conditions, the product of the addition reaction would have only a few microseconds during which it could undergo collision with the diluent gas ($\sim$10 collisions). Hence, it can be concluded that unless the energy rich addition product of the OH-propylene reaction has a lifetime of several hundred microseconds, and would not need more than a few collisions for stabilization, the addition channel would never be detected.Thus, even if the reaction channel for abstraction of an allylic hydrogen by OH was 100 times less than that for addition to the double-bond, the experimental conditions of Slagel,et al.were such that the abstraction

would be the dominant observable reaction path. Finally, we would like to point out that the results obtained by Cvetanavic, et al.[47] in which low intensity photolysis experiments were carried out at high pressures, indicate that addition of OH to the double bond of propylene is the main route for this reaction.

OH + 1-Butene, *cis*-2-Butene, and Tetramethylethylene

The results for these three reactions are also included in Table XIV. Atkinson and Pitts[42] utilized the technique of flash photolysis-resonance fluorescence as in the case of the present work. As noted earlier, Morris and Niki[40] and Pastrana and Carr[43] utilized flow techniques. As can be seen from Table XIV, the results obtained by Atkinson and Pitts for the reactions of OH+1-Butene and OH+*cis*-2-Butene agree with those obtained by us. However, the rate constant for the reaction of OH + 1-Butene obtained by Pastrana and Carr is approximately a factor of two lower than that obtained in this work. We believe that the explanation for this discrepancy lies, partially, in the lower pressures utilized by Pastrana and Carr. As discussed above for the OH-propylene system, we believe that at pressures of 1 Torr the OH-olefin reaction has not reached the high pressure limit. As in the case of OH + 1-Butene, the rate constants for the OH-*cis*-2-Butene and OH-tetramethylethylene reactions obtained by Morris and Niki[40] are very much higher than those obtained by us. This discrepancy would be further enhanced if we were to utilize our value for k_9 relative to which k_{10}, k_{11} and k_{12} were measured. There is, however, a possibility that a significant perturbation in this system due to secondary reactions is responsible for the disagreement with our data.

Atmospheric Implications

In the introduction, the reaction of the hydroxyl radical with hydrocarbons was indicated to be the initial step in the oxidation of hydrocarbons leading to the formation of ozone through a complex sequence of reactions involving NO_x species. The reactions which follow the inital step are believed to be relatively fast. Hence, the effective time before which these hydrocarbons can generate ozone is dictated by the lifetime of the hydrocarbon with respect to its reaction with OH.* This would mean that the confinement of the ozone problem to the hydrocarbon emission region would be governed by the rate of chemical degradation relative to transport. The latter variable, the mass transport, would depend on exact meteorological conditions at, and at least one to two days after, the time of release. The chemical degradation rate can be calculated using available rate constant data and atmospheric modelled and/or measured OH concentrations.

In Table XV we have listed our calculated hydrocarbon lifetimes, under varying conditions, for all the compounds studied during this program. In this case, the destruction rate of a given hydrocarbon is given by

$$-\frac{d[RH]}{dt} = k[OH]_{ave}[RH] \qquad (13)$$

and

$$\tau_e(\text{lifetime}) = \{k[OH]_{ave}^{-1}\} \qquad (14)$$

where $[OH]_{ave}$ is the average OH concentration which has been computed for several different time periods. Thus, the two parameters required to

* This statement is only strictly true for the case of saturated and aromatic hydrocarbons. In the case of highly reactive olefinic hydrocarbons, reaction with ozone is also an important degradation mechanism.

calculate the lifetime are the average steady state OH concentration and the bimolecular rate constant for a given OH-hydrocarbon reaction. The bimolecular rate constant, k, depends on the temperature while the steady state OH concentration varies with the altitude, latitude, season, and the time of day. However, since the value of k for most compounds examined here would vary little over a nominal seasonal temperature change of 0-30 C, we have used a 300K value in all our calculations. OH concentrations were taken both from the quasi-equilibrium modelling calculations of Chang, Wuebbles, and Davis, and from the direct OH measurements reported by Davis et al. at low altitudes (2.1 km). The latter measurements were carried out at approximately high noon at 37° N latitude under summertime conditions (OH = 9 x 10^6 cm^{-1}). Chang,et. al. have calculated steady state OH concentrations as a function of latitude, altitude, season, and time of day; they have also evaluated diurnal averaging factors for different latitudes, altitudes, and seasons of the year.

As seen from Table XV, we have calculated the lifetimes of 14 hydrocarbons under widely different conditions. For those lifetimes which would be longer than the diurnal solar cycle (12 hours in summer and 8 hours in winter), we have used diurnally averaged OH concentrations. From the calculated lifetimes, which vary from less than one hour to as long as a few months, we can classify those hydrocarbons studied into three categories: (1) those which have lifetimes always less than 3 to 5* hours during summer and winter; (2) those which have lifetimes less than 3 to 5 hours in summer but greater than 7 to 9 hours in winter; and (3) those which have lifetimes greater than 7 to 9 hours during summer and winter.

The significance of such a classification is obvious-lifetimes of less than 3 to 5 hours would imply that these hydrocarbons would be degraded essential-

*The number represents the hydrocarbon lifetime required to degrade ∿60% of a 12-hour day's emission (at constant rate) within the same solar day.

TABLE XV. Lifetimes of Hydrocarbons in the Lower Troposphere

Compound	Rate Constant cm^3 $molecule^{-1}$ s^{-1}	30°N Summer 8AM[1],[a](hrs)	30°N Summer 12Noon[2](hrs)	30°N Summer Diurnal[3](hrs)	30°N Winter 12Noon[4](hrs)	30°N Winter Diurnal[5](hrs)	70°N Summer 12Noon[6](hrs)	70°N Summer Diurnal[7](hrs)	37°N Summer 12Noon[8](hrs)
Benzene	1.6×10^{-12}	*	*	42	**	168	*	84	19
Toluene	5.9×10^{-12}	8	5	12	**	47	*	24	5
Ethyl Benzene	8.2×10^{-12}	6	3.5	8	**	34	11	17	4
n-propyl Benzene	5.8×10^{-12}	8	5	12	**	47	*	24	5
isopropyl Benzene	7.75×10^{-12}	5	3.5	9	**	36	12	18	4
o-xylene	1.24×10^{-11}	3.5	2.2	5.5	**	22	7	11	2.5
m-xylene	2.06×10^{-11}	2	1.5	3.5	7	14	4.5	7	1.5
p-xylene	1.07×10^{-11}	4.5	2.5	6.5	**	26	8.5	13	3
Propene	2.63×10^{-11}	2	1.1	3	5.5	11	4	5.5	1
1-Butene	2.94×10^{-11}	1.5	0.9	2	4.5	9	3	4.5	1
cis-2-Butene	4.26×10^{-11}	1	0.7	2	3.5	7	2	3.5	1
Tetramethylethylene	5.69×10^{-11}	0.8	0.5	1.2	2.5	5	1.5	2.5	0.5
Ethylene	6.0×10^{-12}	8	4.6	11.5	**	46	*	23	5
Acetylene	1.65×10^{-13}	*	*	432	**	1680	*	840	192

[1] OH concentration $\sim 6 \times 10^6$ (Ref. 48, Fig. 2)
[2] OH concentration $\sim 1 \times 10^7$ (Ref. 48, Fig. 2)
[3] OH concentration $\sim 4 \times 10^6$ (Ref. 48, Fig. 3)
[4] OH concentration $\sim 2 \times 10^6$ (Ref. 48, Fig. 2)
[5] OH concentration $\sim 1 \times 10^6$ (Ref. 48, Fig. 3)
[6] OH concentration $\sim 3 \times 10^6$ (Ref. 48, Fig. 2)
[7] OH concentration $\sim 2 \times 10^6$ (Ref. 48, Fig. 3)
[8] OH concentration $\sim 9 \times 10^6$ (Ref. 49)

[a] The lifetime at 4:00PM would be the same as at 8:00AM.
* Lifetime >12 hours.
**Lifetime >8 hours.

ly the same day they are relased, thereby making them a local or regional problem depending on exact meteorological conditions. Those hydrocarbons which have lifetimes greater than 7-9 hours would most likely be transported away from the release point, making them a regional or continental problem.

The olefins-propylene, 1-butene, cis-2-butene, and tetramethylethylene-fall into the first category. Especially during summertime conditions, these olefins would be degraded within a few hours. The three xylenes, toluene, ethyl benzene, the two propyl benzenes, and ethylene have lifetimes shorter than the solar day during summer months; therefore, these compounds would effect local areas. However, during winter months, they could be transported long distances. The three xylenes could have either local or regional effects, depending on exact meteorological conditions. Those compounds in the third category, benzene and acetylene, would have very long lifetimes and would be transported long distances.

The results from our calculations once again point out that control strategies for hydrocarbons should be based on detailed calculations which reflect the reactivity of a given hydrocarbon towards OH, the OH concentration level on a local and regional scale, and meteorological conditions. Thus, considerably different strategies could be expected for different sources having different hydrocarbon emissions.

SECTION 5

IDENTIFICATION OF OH-HYDROCARBON REACTION PRODUCTS

OVERVIEW

During the last year of our three year effort involving studies of OH-hydrocarbon reactions, two different laser systems were successfully interfaced with a T.O.F. Bendix mass spectrometer for purposes of investigating the reaction products from OH-hydrocarbon processes. Two different modes of operation for this system were investigated; although neither mode was completely successful, the work did proceed sufficiently far as to make quite clear the potential of this new methodology and the new elements needed to fully realize this potential.

The two basic components in the Georgia Tech system are (1) a T.O.F. mass spectrometer and (2) a high energy pulsed laser. The time-of-flight mass spectrometer operates by separating, in real time, the ions formed in the ion source into groups characterized by their mass to charge ratio. The ions arrive at the magnetic electron multiplier detector in groups separated in time. This process of ionization, separation, and detection is repeated every 100 μs. Hence, this machine has the potential of acquiring 10,000 mass spectra in one second. As indicated above, there are two modes in which we operated the T.O.F. during the present investigation: (a) spectrum acquisition and (b) single ion monitoring. In the first mode of operation, the output of the magnetic electron multiplier (MEM) was constantly gated into the

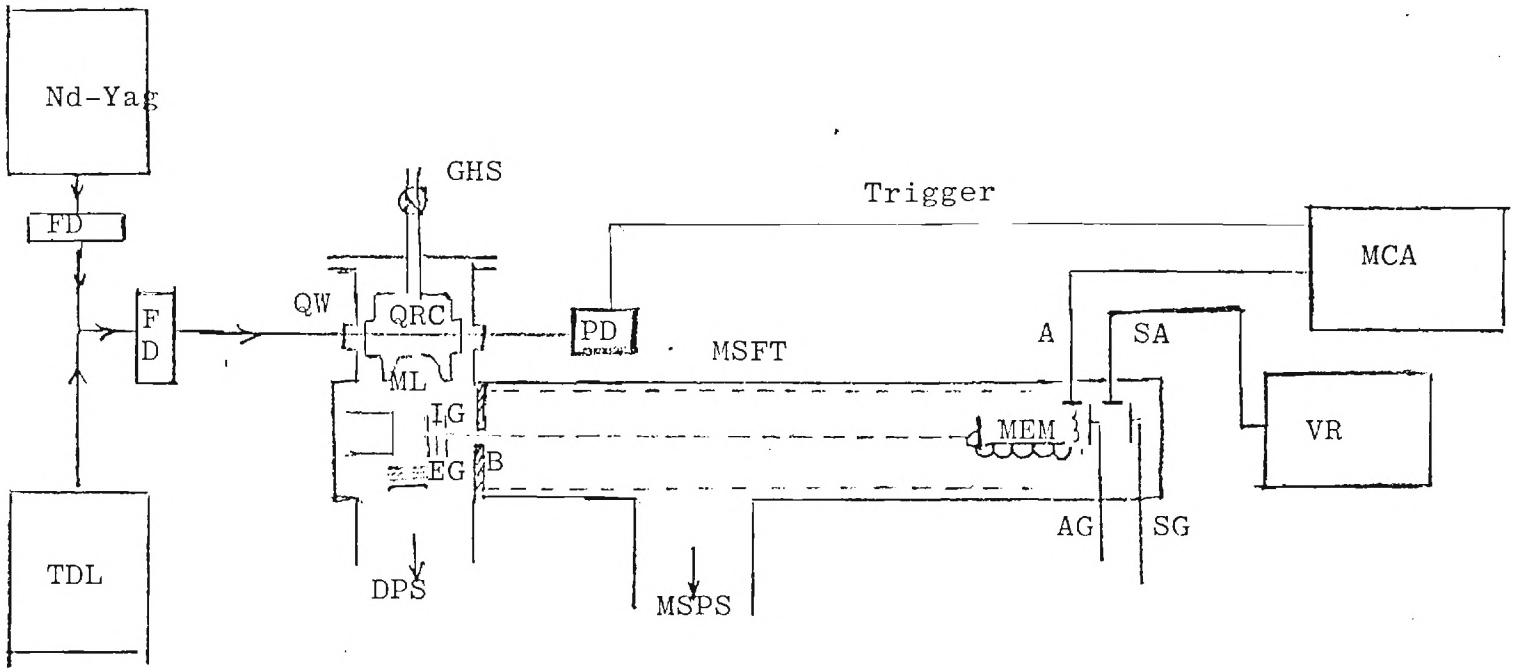
scope anode--the output of this anode being the mass spectrum. The alternative mode of operation was that of diverting the output of the MEM corresponding to one particular mass into the anode. This provided the abundance of a single ion as a function of time with a time resolution of 100 μs.

The second major component in the Georgia Tech system, the photolysis source, consisted of either a Nd-Yag laser or a tunable dye laser. The fundamental output of the Nd-Yag System (ILS-NT-572) was quadrupled to give 2650 Å radiation. This wavelength was suitable to photolyze O_3 to give $O(^1D)$ which, via the $O(^1D)$-H_2 reaction, generated an instantaneous source of OH radicals. Since the first laser system had a repetition rate of 10 pps, the possibility of generating high steady state concentrations of OH reaction products was explored. The second laser, a frequency doubled tunable dye laser, had wavelength output in the spectral region of 2500-3500 Å. Single shot outputs from this system typically ranged from 25-100 mJ, thus making this system suitable for examining the time history of a given reaction product.

EXPERIMENTAL APPROACH

The basic experimental setup is shown in Figure 1. In this system, a quartz reaction cell which was equipped with a molecular leak let a constant fraction of the cell contents effuse into the ionizing region of the T.O.F. mass spectrometer. The mass spectrometer, therefore, acted as a detector which could identify product constituents and measure their relative amounts in the effusion mixture.

For the single ion monitoring mode, the electronic processing of the signal was considerably different than for the steady state operation (mode #1). In the former case, the output of the mass spec anode was monitored by feeding an amplified signal into a multi-channel analyzer (MCA). The MCA was then triggered to start the ion monitoring by a photodiode which was activated by photolyzing laser pulse. Thus, the MCA was set up to record the intensity of a given ion as a function of time. In an effort to further improve on the signal to noise ratio of this system, data from several laser shots was averaged on the MCA.



TDL - Tunable Dye Laser
FD - Frequency Doubling Crystal
Nd-Yag - Neodymium-Yag Laser
GHS - Gas Handling System
QRC - Quartz Reaction Cell
QW - Quartz Window
ML - Molecular leak
EG - Electron Grids
IG - Ion Grid
DPS - Differential Pumping Station

MSFT - Mass Spec Flight Tube
MSPS - Mass Spec Pumping Station
P.D. - Photo-diode
B - Baffle
MEM - Magnetic Electron Multiplier
A - Anode
AG - Anode Gate
SA- Scope Anode
SG - Scope Gate
VR - Visicorder- Recorder
MCA - Multichannel Analyzer

Figure 1. A Schematic Drawing of the Laser-Photolysis--T.O.F. Mass Spectrometer System

EXPERIMENTAL RESULTS

As of this final report, the T.O.F. mass spec-laser photolysis system has been only marginally successful as an operational data collecting system. Even so, we believe that this aspect of the project has been successful in that the operational parameters required to make the system highly successful have now been clearly defined.

The principal chemical system which was examined with the present experimental arrangement was the reaction system ,OH-Toluene. In these experiments, OH radicals were produced by the UV photolysis of O_3 in the presence of H_2. The $O(^1D)$ product resulting from the photolysis of O_3 reacted with H_2 according to the scheme:

$$O(^1D) + H_2 \longrightarrow OH + H$$

$$H + O_3 \longrightarrow OH + O_2 \quad .$$

Tests carried out with ozone-toluene mixtures showed no evidence of a measurable chemical reaction within the time duration of our experiments (i.e., a few minutes). Experimental conditions were also adjusted such that the dominant reaction of OH was with toluene rather than H_2 or O_3 (both are slow processes). To date, we have seen H_2O as a reaction product from the OH-toluene system; but we have not been able to get the sensitivity of the mass spec-laser system high enough to carry out quantitative experiments. The original idea was that of trying to quantitatively assess the fraction of the total OH-toluene reaction process which was abstraction and that which

was addition to the ring. This was to be carried out by comparing the amount of H_2O formed (a product of abstraction only) in the OH-toluene system with that in a second system where only abstraction could occur with H_2O formation (e.g., a reactive saturated hydrocarbon). As stated above, however, a lack of sensitivity precluded such experiments being carried out. In like manner, the low sensitivity of the T.O.F. mass spec also made it impossible to identify any ring addition products produced from the OH-toluene reaction.

In the case of the high rep rate experiments where steady state concentrations of products were to be examined, the low ionization efficiency of the T.O.F. ion source coupled with an oversized molecular leak in the mass spec reaction cell resulted in less than optimum results. In addition, the use of ozone as a source of OH produced further complications since reactive fragments formed from the initial reaction step of OH with toluene could very likely react with O_3. We believe the solution to the above set of problems is 3-fold: (1) the replacement of the original reaction cell with one containing a smaller molecular leak (permitting a higher build-up product concentration in the reaction cell); (2) the elimination of O_3 as a source of OH; and (3) the generation of high concentrations of OH per unit time from the laser.

With regard to the single ion monitoring mode, where in some cases the time history of a species may be examined, the difficulty here was again the inherent inefficiency of the T.O.F. ion source plus an additional problem involving the integration circuits on the output of the MEM. In the present configuration, the T.O.F. electrometer has a time constant sufficiently long that it is signal averaging even when the reaction products from the laser pulse have long been removed from the ionizing region of the mass spec. In effect, this has caused a factor of 20 to 30 loss in sensitivity.

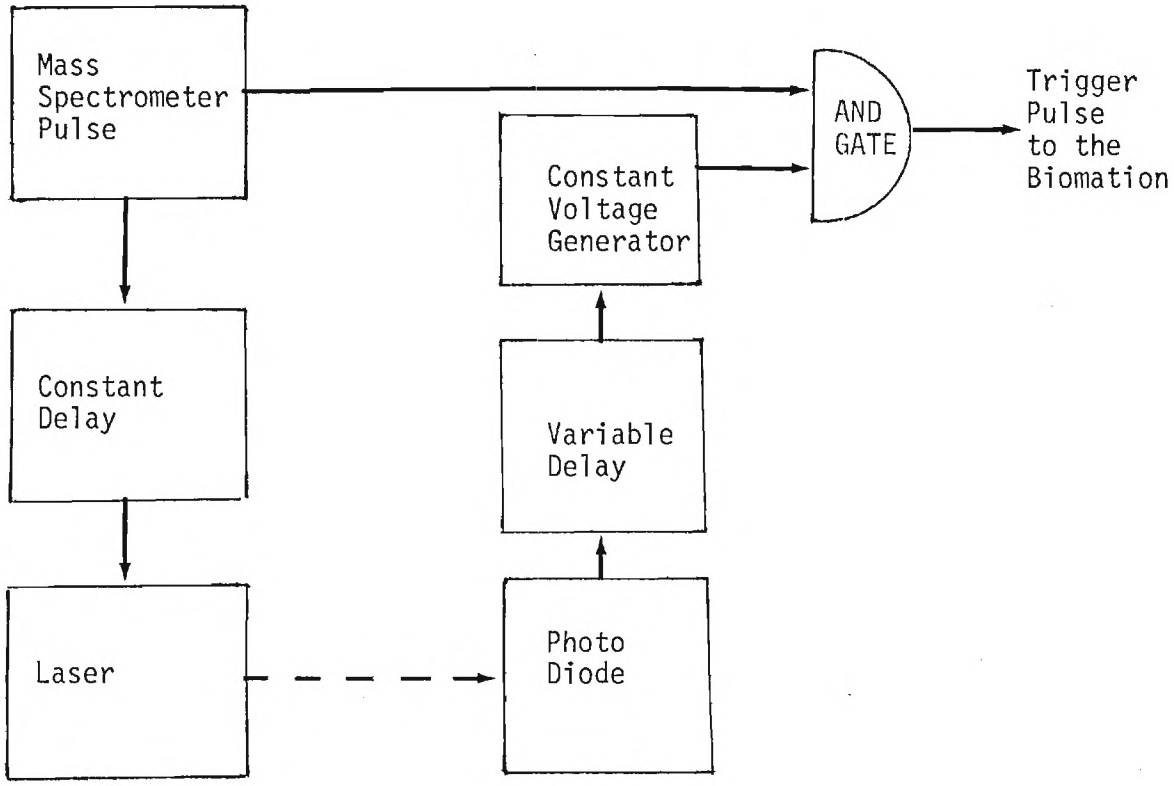
To resolve the two general problems outlined above; namely, low sensitivity and complex secondary chemistry due to the use of O_3 as a source of OH, we have come up with the following recommendations: (1) switch from O_3-H_2 mixtures to H_2O as a ource of OH; (2) increase the OH concentration per laser shot by utilizing an ArCl Eximer laser ($\sim$1700 Å); (3) modify the sampling electronics to permit monitoring of only those mass spec cycles which are synchronized with the laser firing and (4) in the case of the steady state monitoring experiments, employ a reaction cell with a reduced effusion rate.

The switch from O_3-H_2 mixtures to H_2O would prevent the primary reaction products from OH-aromatic reactions from reacting with O_3 to yield non-representative stable secondary reaction products. It also would make possible the study of OH-olefin reaction products since olefin-O_3 mixtures are far too reactive to permit any assessment of the reaction products from OH reactions. A crucial new element required to take advantage of H_2O as an OH source in our studies is the ArCl Eximer laser (point (2) given above). With an output energy of $\sim$25 mJ and a wavelength of $\sim$1700 Å, this vacuum UV laser source would not only permit the use of H_2O as a reliable source of OH, but its high energy output coupled with the high cross section for absorption by H_2O at 1700 Å would also result in an increase in the OH concentration per laser pulse of at least one order of magnitude. The addition of new sampling electronics (i.e., a Biomation 8100 transient recorder) would also improve the sensitivity of the experiment by another order of magnitude by ensuring that only those cycles of the T.O.F. mass spec were processed which correlated with reaction products actually being in the ion source of the mass spectrometer. With a Biomation transient recorder the following sequence of events would occur:

1. The laser would fire and this photolysis flash would initiate the OH-hydrocarbon reaction.
2. The reaction products along with the reactants and the diluent gas would effuse into the path of the ionizing electron beam.
3. The Biomation transient recorder would be used to capture (in 2048 memory locations) the scope anode output wave form generated by a single cycle of the mass spectrometer when the concentration of the products is high.
4. The captured wave form (the mass spectrum) would be transferred to a Northern Scientific signal averager within 25 milliseconds after the termination of the sweep.
5. Within the next five milliseconds the Biomation transient recorder would be cleared and "armed" to accept a new wave form.
6. The next laser flash would trigger the same sequence of events except that the new wave form obtained would be added to the previous wave form that is stored in the Northern Scientific signal averager.

Through this sequence of events, we could signal average as many as 1200 times/second.

The necessary requirements for obtaining a pertinent wave form would be that the laser has fired, the reaction products have effused into the ion source, and the mass spectrometer has just started a new cycle. Hence, the triggering scheme must involve a trigger pulse going to the Biomation transient recorder only after the above events have taken place. For our experiments, we would utilize a triggering scheme as shown below:



The master pulse from the mass spectrometer clock would be suitably delayed (maybe as long as 90 microseconds) and fed into the laser. The laser would fire within a few microseconds after being triggered. The photodiode would detect the laser flash and send a signal to the constant voltage generator box through a variable delay. Once the pulse reaches this box it would set a flag in the And-Gate, thereby partially arming the gate. As soon as the mass spectrometer starts a new cycle, the master pulse would feed a signal into the And-Gate thereby enabling the gate to produce the trigger for the Biomation recorder. By changing the delay between the emergence of the photodiode pulse and the time at which the constant generator sets up a flag in the gate, a mass spectrum characteristic of the reaction products at different reaction times could be obtained. By suitably gating the Biomation

output, we could also monitor the time profile of a single ion intensity. This kind of study could yield kinetic information.

The cost of making the above changes (e.g., buying an Eximer laser and a Biomation transient recorder) has been estimated by us to be $15 to $20K. Obviously, no such funds were available in our grant this year and, with the exception of building a new reaction cell, further experimental progress on the project was slowed considerably during the last two months. We have, however,within the last month, taken action at Georgia Tech which,within the next six months,should make available both an Eximer laser and a Biomation transient recorder. If these elements are obtained as expected, we would want to seriously consider renewing our efforts at OH-Olefin, Aromatic product analysis via the mass spec-laser methodology. In such a case, further funding from EPA would add very measurably to the rate at which new results could be obtained.

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16. ABSTRACT

The flash-photolysis resonance fluorescence technique has been utilized to study the reaction kinetics of hydroxyl radicals with ten aromatic and six olefinic hydrocarbons at 298 K and several diluent gas pressures. The aromatic compounds that were studied include benzene, toluene, ethylbenzene, n-propylbenzene, isopropylbenzene, hexafluorobenzene, n-propyl pentafluorobenzene, o-, m-, and p-xylenes; and the olefins include ethylene, acetylene, propylene, 1-butene, cis-2-butene, and tetramethylethylene. Based on our extensive data on OH-substituted aromatic hydrocarbon reactions, it has been inferred that addition of hydroxyl radicals to the aromatic ring is the dominant reaction in these systems. In the case of OH-olefin reactions, addition of OH to the double bond seems to be a prominent path for the heavier unsaturates. From these rate constant data the lifetimes of all these hydrocarbons in the lower troposphere has been calculated. Utilizing the technique of laser flash photolysis, time-of-flight mass spectrometry, attempts were made to understand the mechanisms involved in the reactions of OH with substituted aromatic hydrocarbons.

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